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Contents of Volume

Number 1

Oxidative Dehydrogenation of Hydrocarbons 1
V K Skarchenko

Condensation of Unsaturated Compounds with Formaldehyde (the Prins Reaction) 17
V I Isagulyants, T G Khaimova, V R Melikyan, S V Pokrovskaya

Electrical and Photoelectric Properties of Organic Polymeric Semiconductors 25
V S Myl'nikov

Precipitation Chromatography 39
A A Lur'e

Structure Formation in Disperse Systems in an Electric Field 53
L G Gindin, A E Vol'pyan

Radiolysis of Solid Inorganic Salts with Oxygen-containing Anions 61
Yu A Zakharov, V A Nevostruev

Autocatalytic and Impedance Phenomena and the Effect of the Physical State of the Solid Product on the Acceleration and Retardation of Reversible Topochemical Reactions with Participation of Solid and Gaseous Reactants 73
E S Vorontsov

Number 2

Astatine 87
V D Nefedov, Yu V Norseev, M A Toropova, V A Khalkin

Physicochemical Properties and Structure of Complex Compounds of Aluminium Hydride 99
N M Alpatova, T N Dymova, Yu M Kessler, O R Osipov

Progress in the Synthesis of Peptides on Polymers 114
V S Vesa

The Structure of Conjugated Open-chain Hydrocarbons 119
E M Popov, G A Kogan

The Masking of Reactions 142
F P Sudakov

Infrared Spectra of Steroids 155
Yu N Levchuk

Number 3

Organoelementary Derivatives of Barenes (Carboranes-10) 173
V I Bregadze, O Yu Okhlobystin

The Chemistry of Manganese Carbonyl 184
K N Anisimov, A A Ioganson, N E Kolobova

γ- and δ-Unsaturated δ-Lactones 198
N P Shusherina, R Ya Levina

Fast Complexing Reactions 209
L I Budarin, K B Yatsimirskii

Influence of Intermolecular and Intramolecular Order on the Infrared Absorption Spectra of Polymers 225
V N Nikitin, B Z Volchek

Number 4

New Information about Oxygen-containing Compounds of Iodine 243
M Drátovský, L Pačesová

γ-Formyl Acids 254
V M Andreev, G P Kugatova-Shemyakina, S A Kazaryan

Progress in the Chemistry of the 1,3-Dioxans 264
A V Bogatskii, N L Garkovik

Progress in the Analytical Chemistry of Non-aqueous Solutions 278
L N Bykova, A P Kreshkov, N A Kazaryan, I D Pevzner

Contrast Intensification in the Electron Microscopy of Polymers 298
E M Belavtseva, K Z Gumargalieva

Water as a Semiconductor 310
V N Maslov, Yu A Zotov

Number 5

Reactions of the Chlorides of Phosphorus Acids with Unsaturated Compounds 317
N A Pudovik, V K Khairullin

The Concept of Electronegativity. Conclusions and Prospects 332
S S Batsanov

Methods of Preparation and Chemical Properties of Aliphatic Halogenonitro-compounds 351
G A Shvekhgeimer, V A Smirnyagin, R A Sadykov, S S Novikov

The Chemistry of Acyl and Sulphonyl Isocyanates, Isothiocyanates, and Isoselenocyanates 363
M O Lozinskii, P S Pel'kis

New Data on Biradicals 376
I D Morozova, M E Dyatkina

Processes Occurring in Solids Under the Action of Powerful Shock Waves 392
A N Dremin, O N Breusov

Application of Electrical Spin Resonance in Chemical Kinetics 402
Ya S Lebedev

Number 6

Oxidation of Sterically Hindered Phenols 421
L M Strigun, L S Vartanyan, N M Emanuel'

Stable Phenoxy-radicals 435
V D Pokhodenko, V A Khizhnyi, V A Bidzilya

Retention of Configuration in Reactions with Opening of an Epoxide Ring 448
A A Akhrem, A M Moiseenkov, V N Dobrynin

Polymerisation of Lactones 463
Yu N Sazanov

Gas Hydrates 469
S Sh Byk, V I Fomina

Synthesis of Technical Tanning Agents 491
Ya P Berkman

Number 7

Organophosphorus Complexones 503
M I Kabachnik, T Ya Medved', N M Dyatlova, O G Arkhipova, M V Rudomino

Structure of Organic Oxygen Compounds of Sulphur 519
Yu A Kolesnik, V V Kozlov

Hydroxyalkylphosphines and Hydroxyalkylphosphine Oxides 532
K A Petrov, V A Parshina

Nitrosochlorination of Alkenes 543
P P Kadzyauskas, N S Zefirov

The Chemistry of Azaindoles [Pyrrolo[2,3]pyridines] 551
L N Yakhontov

Chromatographic Resolution of Racemates on Dissymmetric Sorbents 565
S V Rogozhin, V A Davankov

Gas-chromatographic Methods for Studying the Kinetics of Liquid-phase Reactions 576
V G Berezkin

Number 8

Rearrangements Connected with the Migration of Acyl and Certain Other Groups 587
L V Pavlova, F Yu Rachinskii

Thermal Decomposition of Aliphatic Nitro-compounds 603
G M Nazin, G B Manelis, F I Dubovitskii

Catalysis of Isotope Exchange in Molecular Oxygen and Its Application to the Study of Catalysts 613
G K Boreskov, L A Kasatkina

The Electron Spin Resonance Method in Photochemistry 628
V E Kholmogorov

Application of the Ferromagnetic Resonance Method in the Study of Heterogeneous Catalysts 642
A A Slinkin

Number 9

Martin Izrailevich Kabachnik 655
A M Sladkov

Oxidation of Benzene 656
E T Denisov, D I Metelitsa

Valence Isomers of Benzene 666
I G Bolesov

Methods of Preparation and Properties of Compounds with Unsaturated Groups at the Phosphorus Atom 670
V K Promonenkov, S Z Ivin

Copolymerisation of Cyclic Compounds 681
T M Frunze, V V Kurashev

Metal Ammonium Phosphates and Their New Applications 693
L M Lapina

Separation of Rare-earth Elements by Electrolysis at a Mercury Cathode 701
G M Kolesov, L N Pankratova

Some Electrochemical Properties of Mercury 710
E F Speranskaya, T G Pokhvalitova

Non-adiabatic Processes of Energy Transfer in Gases 716
E E Nikitin

The "Memory" Effect in Semiconductor Adsorbents and Catalysts during Radiation 724
F F Vol'kenshtein, V G Baru

Countercurrent Fractional Crystallisation 728
Yu A Chikin, V I Lukhovitskii

Number 10

Isotopic Exchange of Hydrogen in Aromatic Complexes of the Transition Metals 737
V N Setkina, D N Kursanov

Copper and Silver Acetylides in Organic Synthesis 748
A M Sladkov, L Yu Ukhin

Dipole Moments and the Structure of π-Complexes of Metals 763
A D Garnovskii, O S Osipov, V I Minkin

Progress in the Synthesis of Perfumes Based on Pinenes 779
Y - Naves

Dimerisation of Alkenes 789
V Sh Fel'dblyum, N V Obeshchalova

Nuclear Magnetic Resonance in Radicals and in Radical Reactions 798
A L Buchachenko, N A Sysoeva

Methods of Thermokinetic Analysis of Chemical Reactions 812
V S Livshits

The Differentiating Action of Oxygen-containing Solvents on the Strengths of Acids 818
V I Dulova, N V Lichkova, L P Ivleva

Number 11

L.Ya.Karpov Physicochemical Scientific Research Institute of the Order of the Red Banner of Labour. 833
A M Sladkov

Active Centres in the Polymerisation of Hydrocarbon Monomers by Anionic Coordination 834
S S Medvedev

Relative Strength of CH Acids 845
A I Shatenshtein, I O Shapiro

Highly Disperse Aerosols 855
N A Fuks, A G Sutugin

Formation of Donor–Acceptor Complexes 863
E N Gur'yanova

Organomagnesium Compounds and Their Complexes as Polymerisation Initiators 874
B L Erusalimskii, I G Krasnosel'skaya, I V Kulevskaya

Dependence of Thermal Stability of Polymers on Their Chemical Structure 885
V V Korshak, S V Vinogradova

Synthesis of Vinyl Ethers Containing Functional Groups and Heteroatoms 907
M F Shostakovskii, B A Trofimov, A S Atavin, V I Lavrov

Synthesis of Ion-exchange Membranes 920
O D Savenko, F T Shostak, B N Laskorin

Number 12

Sulphur-containing Organic Compounds of Boron 935
B M Mikhailov

Electron Transfer as an Elementary Act of Organic Reactions 954
K A Bilevich, O Yu Okhlobystin

Stereospecific Catalysis in the Field of Optically Active Polymers 969
E I Klabunovskii

Macromolecular Complexes as Chemical Reaction Catalysts 984
S L Davydova, N A Plate, V A Kargin

The Inhomogeneity of Copotymers with Respect to Composition 996
V A Myagchenkov, S Ya Frenkel'

The Dependence of the Mechanism of the Hydrolysis, Trans-esterification, and Trans-etherification of α,β-Alkenyl Ethers and Esters on Their Structure 1009
A F Rekasheva

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Oxidative Dehydrogenation of Hydrocarbons

V.K.Skarchenko

CONTENTS

I. Introduction	1
II. Oxidative dehydrogenation of olefins	1
1. Chemical composition of the catalysts	2
2. Kinetics	3
3. The mechanism of oxidative dehydrogenation	5
III. Oxidative dehydrogenation of saturated hydrocarbons	8
1. Dehydrogenation in the presence of oxygen	8
2. Dehydrogenation in the presence of iodine	10
3. Dehydrogenation in the presence of oxygen and small amounts of iodine	12

I. INTRODUCTION

In recent years the oxidative dehydrogenation reactions, whereby olefins and diene monomers can be made from the corresponding more saturated hydrocarbons, have been attracting increasing attention. The essential feature of the oxidative dehydrogenation reaction consists in the partial oxidation of the hydrogen in the organic molecules without affecting the hydrocarbon skeleton. In the usual dehydrogenation of saturated hydrocarbons the conversion of the latter into unsaturated hydrocarbons is limited by the position of the equilibrium in the reversible reaction

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n-2} + 2H_2. \quad (1)$$

The extent of dehydrogenation of hydrocarbons can be sharply increased if the equilibrium is displaced by binding the hydrogen in the form of water, for example:

$$C_nH_{2n+2} + O_2 \rightleftarrows C_nH_{2n-2} + 2H_2O \quad (2)$$

or as hydrogen iodide:

$$C_nH_{2n+2} + 2I_2 \rightleftarrows C_nH_{2n-2} + 4HI. \quad (3)$$

Iodine is much more active as a dehydrogenating agent than oxygen and oxidative dehydrogenation using iodine can be of practical interest in those cases where the dehydrogenation is coupled with an effective iodine regeneration process. The iodine consumed in reaction (3) can be regenerated, for example, by the oxidation of the resulting hydrogen iodide with oxygen:

$$2HI + {}^1/_2O_2 \rightarrow H_2O + I_2 \quad (4)$$

or, as is usually done, the hydrogen iodide is first trapped by solid acceptors, for example, metal oxides, with formation of the corresponding iodides:

$$MO + 2HI \rightleftarrows H_2O + MI_2. \quad (5)$$

On heating in a stream of air, metal iodides readily decompose with evolution of elemental iodine:

$$MI_2 + {}^1/_2O_2 \rightarrow MO + I_2. \quad (6)$$

In contrast to normal dehydrogenation, oxidative dehydrogenation reactions are exothermic.

II. OXIDATIVE DEHYDROGENATION OF OLEFINS

A considerable amount of the available literature on the oxidative dehydrogenation of olefins refers to the conversion of n-butenes into divinyl and of isopentenes into isoprene. The oxidative dehydrogenation of mono-olefins into diolefins is a typical heterogeneous catalytic reaction.

Under certain conditions a high selectivity of the reaction

$$C_4H_8 + {}^1/_2O_2 \rightleftarrows C_4H_6 + H_2O \qquad (7)$$

is attained on suitable catalysts. Small amounts of furan, carbon monoxide, carbon dioxide, acetone, propene, ethylene, formaldehyde, and other substances are formed as side-products. Reaction (7) is an oxidative process and not dehydrogenation with subsequent oxidation of hydrogen. Hydrogen is either completely absent from the reaction system or is not oxidised under the experimental conditions. The oxidation of butane under these conditions is much slower than that of butenes and it is converted preferentially into carbon monoxide and carbon dioxide. Under the normal experimental conditions for the oxidative dehydrogenation of n-butenes into divinyl, thermal reactions virtually do not occur in a Pyrex reactor; a steel reactor favours the formation of carbon dioxide.

1. CHEMICAL COMPOSITION OF THE CATALYSTS

A fairly large number of catalyst recipes have been proposed for the dehydrogenation of mono-olefins in the presence of oxygen: molybdates or tungstates of bismuth [1-7], cobalt, vanadium, tin, titanium [8], tellurium [9], phosphoric acid on alumina [3,5,10], phosphates of bismuth, iron [11,12], strontium, nickel, chromium, calcium [13,14], tungsten, vanadium [15], and indium [16], phosphomolybdate and phosphotungstate of bismuth [17,18], mixed oxides of antimony and tin [3-5,19-24], mixed oxides of titanium [25], mixed oxides of tin and arsenic with selenium and tellurium [19], mixed oxides of iron with aluminium and chromium [26], basic halides of iron, cobalt, magnesium, and manganese [27,28], gold and platinum [29], and others [30].

The application of certain solid catalysts is combined with the introduction into the reaction zone of halogen-containing [31-42] or sulphur-containing [43-46] compounds, which decompose under the reaction conditions with formation of halogens or sulphur dioxide. Thus mixed and pure oxides of iron, cobalt, nickel, manganese, vanadium, molybdenum, bismuth, tin, cadmium, and copper, magnesium phosphate, and many other compounds are recommended for the oxidative dehydrogenation of mono-olefins in the presence of halogen- or sulphur-containing compounds.

Despite the large number of catalysts tested, relatively few data have been published which would permit their comparison. Some typical results of tests of catalysts under optimum conditions are presented in Table 1. The data in Table 1 permit only a very restricted quantitative comparison of the catalysts, since the conditions of the tests, the composition of the raw material, and the method of preparation and treatment of the catalysts were not the same in most of the studies quoted. The yield of diolefins on a molybdenum–bismuth catalyst in the oxidative dehydrogenation of individual butene isomers increases in the series *trans*-but-2-ene, *cis*-but-2-ene, and but-1-ene, and in the dehydrogenation of isopentenes it increases in the series 2-methylbut-1-ene, 2-methylbut-2-ene, and 3-methylbut-1-ene.

High yields of divinyl (65–74%) with a selectivity of 83–91% were attained on many catalysts of various compositions. The same catalysts as those for the dehydrogenation of n-butenes proved to be preferable for the oxidative dehydrogenation of isopentenes to isoprene. The fact that on certain catalysts (mixed oxides of antimony and tin, phosphates) high yields of diolefins are attained at temperatures not higher than 400°C is also striking. The highest yields of diolefins and the highest selectivity are observed in the presence of iodine- and sulphur-containing compounds. Evidently, these additives themselves play a significant if not the main role in the dehydrogenation reaction. Fairly high yields of divinyl were obtained on quartz and silica gel, these catalysts being markedly inferior to those listed in Table 1 only as regards selectivity.

Kolobikhin and Emel'yanova [53] investigated the effect of the proportions of bismuth and molybdenum and also of the total content of bismuth and molybdenum oxides in the catalyst on its dehydrogenating capacity. The catalysts were made by impregnating silica gel for 1 h at room temperature with a complex solution of bismuth nitrate and ammonium molybdate in nitric acid. The optimum composition of the catalyst corresponded to the atomic ratio Bi : Mo = 0.7–0.9 and 18–20 wt.% of bismuth and molybdenum oxides. The silica gel was treated with steam and had a specific surface of 64 $m^2 g^{-1}$ and a pore volume of 0.82 $cm^3 g^{-1}$. An analogous study of bismuth–tungsten catalysts [54] showed that catalysts with the atomic ratio Bi : W = 0.67–1.5 exhibited the highest activity. The addition of phosphorus up to atomic proportions Bi : P : W = 12 : 1 : 12 increases the yields of divinyl.

Table 1. Oxidative dehydrogenation of certain unsaturated hydrocarbons on catalysts of various chemical compositions.

Catalyst	Initial hydrocarbon	Temperature, °C	Moles per mole of hydrocarbon: of oxygen	Moles per mole of hydrocarbon: of nitrogen, water, or other diluent	Yield of diolefins, %: with respect to starting material	Yield of diolefins, %: with respect to product	References
Bismuth molybdate	but-1-ene	460	1	4	74	91	1
Bismuth molybdate	*cis*-but-2-ene	494	1	4	70	82	1
Bismuth molybdate	*trans*-but-2-ene	493	1	4	66	83	1
Mixed Sb and Sn oxides	but-1-ene	405	1	8	69	90	20
Mixed Mo and Te oxides	but-1-ene	440	1	4	67	90	47
Ni, Ca, and Cr phosphates	but-1-ene	670	1	18	57	83	13
Bismuth tungstate	but-1-ene	470	1	4	51	78	6
Bismuth phosphate	but-1-ene	500	1	2	46	80	11
Indium phosphate	but-1-ene	490			44	61	16
V and K sulphates with 0.4 mole of $(NH_4)_2SO_3$*	but-1-ene	680	0.1	2.4	79	89	43
Ni + ceramic with 0.097 mole of NH_4I *	but-2-ene	602	0.8	14.6	87	99	42
Bismuth molybdate	n-butenes	500	0.8	4	66	88	2
Basic Fe bromides	n-butenes	450	0.5	5.5	67	86	27
Bi and Fe phosphates	n-butenes	350			66	83	12
Mixed Sb and Sn oxides	n-butenes	370	1	8	65	88	25
Mixed Group VIII and IV oxides **	n-butenes	430	0.8	2.3	47	76	48,49
Quartz	n-butenes	550	0.5	5	48	48	50
Silica gel	n-butenes	550	0.5	5	44	45	50
V and K sulphates with 0.4 mole of $(NH_4)_2SO_3$ *	isopentenes	680	0.1	2.4	64	74	43
Vanadium pentoxide with 0.0275 mole of 1-iodo-3-methylbutane *	2-methylbut-2-ene	500	0.8	12	91	94	36
Bi and Fe phosphates	2-methylbut-2-ene				47	64	12
Mixed Sb and Sn oxides	2-methylbut-2-ene	380	2	17	40		25
Bi phosphomolybdate	isopentenes	510	1	24	36	63	51
Bi phosphotungstate	isopentenes	510	1,4	26	33	66	51
Bismuth molybdate	3-methylbut-1-ene	500	3	6	45	70	52
Bismuth molybdate	2-methylbut-1-ene	500	3	6	36	60	52
Bismuth molybdate	2-methylbut-2-ene	520	3	6	39	60	52
Cobalt molybdate	isopentenes	510	1.4	36	30	54	51
Phosphoric acid on Al_2O_3	2-methylbut-2-ene	450	1.1	9	56		10
Bismuth molybdate	ethylbenzene	550	0.3	1.2	23***		7

* The iodine- and sulphur-containing compounds were introduced into the reaction together with the initial hydrocarbon. The table indicates the number of moles of the additive per mole of the hydrocarbon.

** Composition of the catalyst not published.

*** Yield of styrene.

According to the data of other workers [55,56], the optimum composition of the molybdenum–bismuth catalyst is in the range Mo : Bi = 1–2 and probably depends on the nature of the carrier and the method of preparation of the catalyst. The extent of formation of carbon dioxide increases with the bismuth content in the specimen. Therefore the highest selectivity is attained in the presence of an excess of molybdenum in the catalyst (Mo : Bi = 2–4).

Kolobikhin and coworkers [57] investigated the effect of the pore structure in the carrier for the bismuth–molybdenum catalyst. They tested four silica gels of various brands with specific surfaces between 680 and 64 $m^2 g^{-1}$. As the specific surface of the silica gel increased, there was a corresponding increase in the conversion of n-butene but the selectivity with respect to divinyl fell. The decrease of the selectivity can probably be explained by the diffusion-dependent inhibition of the reactions on finely porous specimens [58], the divinyl formed undergoing secondary reactions.

2. KINETICS

a. Reaction Temperature

Depending on the properties of the catalyst and the reaction conditions, the maximum yields of divinyl and isoprene in the oxidative dehydrogenation of the corresponding mono-olefins were observed at 370–570°C. [1,18,59–62] With increase of temperature above the optimum value, the yields of the secondary reaction products, mainly carbon dioxide and also furan and carbonyl compounds [62], also rise.

According to the data of Tsailingol'd et al. [63], in the temperature range 410–490°C the temperature dependence of the rate constants for the overall conversion of n-butenes on the bismuth–molybdenum catalyst is defined by the expression

$$\lg k = -\frac{13900}{4.545T} + 3.18 \qquad (8)$$

Thus the apparent activation energy is 13.9 kcal $mole^{-1}$. According to the data of other workers, this quantity is much higher. Thus, according to Adams [1], it is 26 kcal $mole^{-1}$ for but-1-ene at 345–500°C. The apparent activation energies for the oxidative dehydrogenation and combustion of isopentenes at 475–525°C are approximately 21 kcal $mole^{-1}$. [64] At 340–390°C about 40 kcal $mole^{-1}$ was obtained for the oxidative dehydrogenation of but-1-ene [56]. As the temperature is increased above 390°C, the activation energy falls appreciably, probably because of the diffusion-dependent inhibition of the reaction [58].

b. Duration of Contact

Examination of data on the reaction of n-butenes on bismuth molybdate deposited on silica gel as a function of space velocity [53] shows that, other conditions being equal, the maximum yield of divinyl depends on the composition of the catalyst. On a specimen containing 35% of the active substance the same conversion is attained for a shorter contact time than on a specimen containing 13% of bismuth molybdate. With increase in contact time, the difference between the yields of divinyl and the selectivities of all the specimens decrease.

When the time of contact is increased above the optimum value, the yields of divinyl decrease due to secondary reactions, as happens on raising the temperature.

c. Concentrations of the Starting Materials

When the molar ratio oxygen : hydrocarbon is raised from 0.1 to 1, the yields of divinyl and isoprene in the dehydrogenation of the corresponding mono-olefins increase, but there is also an increase in the amount of oxygen-containing side-products formed: carbon dioxide, furan, and carbonyl and carboxy-compounds [53,54,62,65]. A necessary condition for the maximum yield of divinyl is the presence of oxygen in the effluent gases. The lower the oxygen to butenes ratio the greater is the decrease of the activity of the catalyst with time [53].

According to the data of Mel'nik and Tyuryaev [66], the initial "instantaneous" activity of the catalyst is independent of the concentration of oxygen, which determines only the extent of the subsequent fall of activity with time. The decrease of the yields of divinyl with time can be accounted for mainly by the change in the phase composition of the bismuth–molybdenum catalyst and not only by the deposition of carbonaceous substances. Indeed at low oxygen to butenes ratios the amount of divinyl and carbon dioxide formed in the first minutes of the reaction is greater than the amount which could form if all the oxygen supplied were utilised [66]. The decreased activity of the molybdenum–bismuth catalyst on reducing its oxygen content was demonstrated also by direct experiments with partial reduction of the catalyst [63]. On partial reduction, the higher oxides of bismuth and molybdenum are converted into lower oxides, as a result of which the activity of the catalyst decreases. According to the results of another investigation [67], the lattice oxygen is consumed during the reaction even when oxygen is present in a large excess in the reaction mixture.

Thus the oxygen of the catalyst itself participates in reactions involving the formation of divinyl and carbon dioxide. The oxygen in the gas phase has a dual function in the oxidative dehydrogenation process: to maintain the active oxidised form of the catalyst and to prevent coke formation. In order to ensure the presence of oxygen in the effluent gases in the usual flow-type reactor with a stationary catalyst bed, it is necessary to supply a considerable excess of oxygen at the inlet, but this leads to a decrease of selectivity due to formation of oxygen-containing compounds. Therefore reaction systems with internal mixing are preferred [68] for the oxidative dehydrogenation of olefins. Indeed, in a reactor with a suspended catalyst layer, more effective oxidative dehydrogenation of butenes was achieved than in a reactor with a stationary catalyst bed [68].

All that has been said so far about the effect of the concentration of oxygen applies to the region of low oxygen concentrations, up to the ratio oxygen : butenes = 0.8–1.0. When the oxygen : butenes ratio is increased to values in excess of unity, a change of oxygen concentration no longer has an appreciable effect on the yields of divinyl on the bismuth–molybdenum catalyst.

Tsailingol'd and coworkers [63] investigated the kinetics of dehydrogenation on the bismuth–molybdenum catalyst by a flow-circulation method at 410–490°C. The concentration of oxygen was varied in the range between 0.30 and 6.7 mole % and that of n-butenes between 2.55 and 18.60 mole %. An increase of the concentration of oxygen above 1–2% (at n-butene concentrations in the range 4–5 mole %) did not have an appreciable effect on the rate of the reactions, i.e. in this concentration range the reaction

was of zero order with respect to oxygen. The order of the reaction with respect to oxygen at lower contents of the latter in the system was not established. When the oxygen concentrations are not too low, the rate ω_1 of the overall conversion of n-butenes is given by the expression:

$$\omega_1 = \frac{k_1 P_{C_4H_8}}{1+aP_{C_4H_8}}, \quad (9)$$

where k_1 is the rate constant for the overall conversion and a a constant which varies with temperature.

Adams and coworkers [1] investigated the kinetics of the dehydrogenation of individual n-butene isomers on the bismuth–molybdenum catalyst in a flow-type reactor. The overall conversion of each n-butene is described by a first-order equation with respect to the butenes. The rate of reaction at 460°C is several times higher than those of but-2-enes, of which the *cis*-isomer is more reactive than the *trans*-isomer.

The kinetics of the oxidative dehydrogenation of mono-olefins with a carbon chain of more than four atoms is described by equations more complex than Eqn. (9).. The principal differences are the dependence of the reaction rate on the concentration of oxygen and inhibition by products. Thus, according to Adams [69], we have for pent-1-ene

$$\omega_1 = \frac{aP_{\text{hydrocarb}}P_{O_2}^{1/2}}{1+bP_{O_2}^{1/2}+dP_{\text{diene}}}, \quad (10)$$

where a, b, and d are constants.

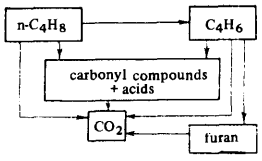
d. Effect of Reaction Products and Diluents

Dilution of butenes with water in proportions of 1 : 10 leads to increase yields of divinyl on the bismuth–molybdenum catalyst. The selectivity then changes much less [54]. Dilution with water in order to optimise the process is recommended also for other catalysts [13,25,70].

With constant concentrations of butenes and oxygen, an increase of the concentration of water from 0 to 40 mole % at 410–470°C does not have an appreciable effect on the rate of reaction on the bismuth–molybdenum catalyst [63]. The same results are obtained when the concentration of carbon dioxide is changed approximately by a factor of 20 and that of divinyl by a factor of six. The dehydrogenation of mono-olefins with a large number of carbon atoms in the chain is inhibited by the products—diolefins [see Eqn. (10)]. According to Alkhazov and coworkers [71], the addition of isobutene also has an inhibiting effect in the dehydrogenation of isopentenes.

The rate of oxidation of divinyl to carbon dioxide on bismuth molybdate is described by a first-order equation with respect to divinyl and a zero-order equation with respect to oxygen [63], amounting under conditions of oxidative dehydrogenation to approximately one-twentieth of the rate of conversion of but-1-ene into divinyl [1], and is thus comparable to the rate of conversion of butenes into carbon monoxide and carbon dioxide. Therefore the carbon dioxide obtained in oxidative dehydrogenation must be regarded as formed partly from divinyl.

The formation of side-products in oxidative dehydrogenation on the bismuth–molybdenum catalyst can be represented by a parallel-consecutive reaction scheme [62]:



Depending on the nature of the catalyst, one or other side-product predominates. Thus, on the iron–zinc catalyst [72], cracking is the principal side-reaction.

e. Isomerisation

The oxidative dehydrogenation of butenes on the bismuth–molybdenum catalyst is accompanied by a change in isomeric composition: the amount of but-1-ene decreases and that of but-2-enes either increases or changes little, while the *cis*-but-2-ene : *trans*-but-2-ene ratio decreases [73]. This is due to the different reactivities of the individual isomers, which decrease in the series but-1-ene > *cis*-but-2-ene > *trans*-but-2-ene. The rate of oxidative dehydrogenation of isopentenes decreases in the series 3-methylbut-1-ene > 2-methylbut-1-ene > 2-methylbut-2-ene [52].

The change in the isomeric composition of mono-olfeins can also be attributed to isomerisation reactions which occur on many catalysts. The rate of the isomerisation reactions depends on the nature of the catalyst. According to Roginskii and coworkers [74,75], the degree of isomerisation of but-1-ene to but-2-ene on the bismuth–molybdenum catalyst without carrier is very low, while for bismuth phosphomolybdate on a carrier the isomerisation is fairly extensive under the conditions of oxidative dehydrogenation.

Table 2. Relative reactivities of olefins in their oxidation on bismuth molybdate at 460°C.

Initial olefin	Main product	Reactivity with respect to the main product referred to	
		one molecule	one hydrogen atom in the allyl position
Propene	acrolein	0.11	0.037
cis-But-2-ene	butadiene	0.26	0.043
trans-But-2-ene	butadiene	0.19	0.032
Isobutene	methacrolein	0.50	0.08
But-1-ene	butadiene	1.00	0.5
2-Methylbut-2-ene	isoprene	2.7	0.3
Pent-1-ene	pentadiene	1.38	0.69
4-Methylpent-1-ene	methylpentadiene	1.6	0.8
Pent-2-ene	pentadiene	0.43	0.086
2-Ethylhex-1-ene	C_8H_{14}	2.8	0.7
3-Methylbut-1-ene	isoprene	2.7	2.7
3-Methylpent-1-ene	methylpentadiene	1.9	1.9
3-Ethylpent-1-ene	C_7H_{12}	1.4	1.4

Studies of the dependence of the isomerising capacity of bismuth–molybdenum catalysts on the Mo : Bi ratio have shown that the rate of isomerisation is highest on molybdenum oxide [55,56]. Isomerisation is not observed under the conditions of oxidative dehydrogenation on a catalyst comprising Group VIII oxides [76].

f. Effect of the Structure of the Hydrocarbons

The unequal reactivities of the individual isomers in oxidative dehydrogenation were pointed out above. Table 2 presents the results of Adams [69] obtained in a study of the comparative reactivities of individual C_3–C_8 hydrocarbons. The reactivities are expressed in relative units with respect to but-1-ene. The reactivity of the allyl C–H bonds increases in the series primary < secondary < tertiary.

Substitution at any vinyl carbon atom increases the reactivity of the olefin. An increase of chain length increases the reactivity of the secondary allyl hydrogen atom (but-1-ene < pent-1-ene < 4-methylpent-1-ene), but reduces the reactivity of the tertiary allyl hydrogen atom (3-methylbut-1-ene > 3-methylpent-1-ene > 3-ethylpent-1-ene).

In the oxidation on bismuth molybdate of molecules which contain less than four carbon atoms in the chain (propene, isobutene) unsaturated aldehydes are formed instead of diolefins. In the reaction of mono-olefins which are readily dehydrogenated to diolefins, carbonyl compounds are formed as side-products. Considerable amounts of mono-unsaturated aldehydes are obtained in the oxidation of mono-subtituted isobutenes.

Certain deviations from the above behaviour can be quite naturally explained. For example, cyclopentene is converted only into total-oxidation products, probably due to the exceptionally high reactivity of cyclopentadiene. Conjugated diolefins are formed from the same molecule at a much higher rate than conjugated olefinic aldehydes.

As the number of carbon atoms in the molecule increases, the degree of inhibition by reaction products (diolefins and aldehydes) also becomes more pronounced. Inhibition by products is shown mainly in a reduction of activity without a significant change in the selectivity of the catalyst.

3. THE MECHANISM OF OXIDATIVE DEHYDROGENATION

a. Similarity of the Oxidative Dehydrogenation of n-Butenes to the Oxidation of Propene to Acrolein and Oxidative Ammonolysis

There exists a profound analogy between the oxidative dehydrogenation of butenes,

$$C_4H_8 + {}^1/_2O_2 \rightleftarrows C_4H_6 + H_2O\,, \qquad (7)$$

the oxidation of propene to the unsaturated aldehyde acrolein,

$$C_3H_6 + O_2 \rightleftarrows C_3H_4O + H_2O\,, \qquad (11)$$

and oxidative ammonolysis of propene with formation of acrylonitrile:

$$C_3H_6 + 1.5O_2 + NH_3 \rightleftarrows C_3H_3N + 3\,H_2O\,. \qquad (12)$$

All the above reactions take place readily on bismuth molybdate. Over a considerable concentration range their rates on this catalyst are described by a first-order equation with respect to the initial mono-olefin and a zero-order equation with respect to oxygen [77,78]. In all the reactions the activity of the catalyst falls in the presence of a deficiency of oxygen, the temperature variation of the yields of acrolein and divinyl in reactions (7) and (11) is approximately the same, the apparent activation energies for these reactions are similar [1], and the kinetic isotope effects in the conversion of deuteriated propene into acrolein and acrylonitrile are also equal [77].

Reactions (7), (11), and (12) have common features: (a) the initial hydrocarbon molecule contains at least one C=C double bond which is not dissociated during the reaction; (b) at least one of the aliphatic C–H bonds dissociated in the reaction is allylic. Transition-metal oxides catalyse these reactions which are sometimes referred to as allyl oxidative reactions.

By the time extensive studies on the oxidative dehydrogenation of olefins began, the oxidation of propene to acrolein had been largely investigated and this plays a definite role in the elucidation of the mechanism of oxidative dehydrogenation. The similarity of the kinetics of reactions (7), (11), and (12) shows that they have a common rate-limiting stage. The first order with respect to the olefin and the zero order with respect to oxygen when $P_{O_2} > (P_{O_2})_{min}$ are evidence that the olefin must take part in the rate-limiting stage.

b. The Mechanism of the Oxidation of Propene to Acrolein

Adsorption of the reactants. According to modern data, the reaction between propene and oxygen takes place on the surface of the catalyst. Both reactants are fairly readily adsorbed on the surface of catalysts such as molybdenum or bismuth oxides. The adsorption of oxygen is at least partially accompanied by dissociation by the active surface centres L:

$$O_2 + 2L \rightleftarrows 2L{-}\dot{O} \qquad (13)$$

The adsorption of propene on the bismuth–molybdenum catalyst is accompanied by dissociation and probably takes place on two surface adsorption centres.

It may be supposed, for example [78], that the transition state preceding dissociation is produced on interaction between a propene molecule and two active centres in which a surface π-complex between one active catalyst centre and the double bond of the propene, on the one hand, and a hydrogen of the methyl group and a second catalyst active centre, on the other, is formed:

$$H_2C{=}CH{-}CH_3 + L_1 + L_2 \rightleftarrows \left\{\begin{matrix} H_2C{=}CH-CH_2 \cdots H \\ \vdots \qquad\qquad \vdots \\ L_1 \qquad\qquad L_2 \end{matrix}\right\} \qquad (14)$$

The transition structure produced as a result of the weakening of the C–H bond in the methyl group is capable of dissociation:

$$\left\{\begin{matrix} H_2C{=}CH{-}CH_2 \cdots H \\ \vdots \qquad\qquad \vdots \\ L_1 \qquad\qquad L_2 \end{matrix}\right\} \rightarrow \underbrace{H_2C \cdots CH \cdots CH_2}_{L_1} + \underset{L_2}{H} \qquad (15)$$

Experimental confirmation. The above picture is in broad outline confirmed by the experimental data obtained in the study of the chemisorption of propene and the oxidation and oxidative ammonolysis of propene labelled with radioactive carbon and deuterium. It is virtually no longer possible to investigate the adsorption of propene at 300°C due to its decomposition on the surface of the bismuth–molybdenum catalyst [79]. Sachtler and De Boer [80] studied the oxidation on the bismuth–molybdenum catalyst of [1-^{14}C]-, [2-^{14}C]-, and [3-^{14}C]-propenes to acrolein. The product was decomposed photochemically into ethylene and carbon monoxide:

$$H_2C{=}CH{-}CHO \rightarrow H_2C{=}CH_2 + CO\,. \qquad (16)$$

The results obtained suggest that the carbon atom of the aldehyde group originates with equal probability both from the methyl and methylene groups of the initial propene. The studies on the oxidation of [1-^{13}C]-propenes on a deuteriated bismuth phosphomolybdate catalyst [81] and of [1-D]-propene and [3-D]propene on bismuth molybdate [77] also led to the conclusion that both terminal carbon atoms are equivalent.

Further reactions. The surface hydrocarbon complex $L_1(CH_2 \cdots CH \cdots CH_2)$ is capable of further reactions, in particular of losing another hydrogen atom or of

combining with oxygen. The formation of acrolein can occur as a result of the following reactions, for example:

$$L_1(CH_2 \cdots CH \cdots CH_2) + L-\dot{O} \rightarrow L_1(CH_2 \cdots CH \cdots CH) + L-OH, \quad (17)$$

$$L_1(CH_2 \cdots CH \cdots CH) + L-\dot{O} \rightarrow L_1(CH_2{=}CH{-}CHO) + L, \quad (18)$$

$$L_1(CH_2{=}CH{-}CHO) \leftrightarrows CH_2{=}CH{-}CHO + L_1, \quad (19)$$

or the surface unsaturated-hydrocarbon complex passes through intermediate stages involving isomerisation to surface radicals, for example:

$$L_1(CH_2 \cdots CH \cdots CH) \rightarrow L_1-\dot{C}H-CH=\dot{C}H_2 \xrightarrow{+L-\dot{O}} CH_2{=}CH{-}CHO. \quad (20)$$

The above hypotheses concerning the possible mechanism of the conversion of the adsorbed allyl radical into acrolein are consistent with the measurements of the kinetic isotope effects in the oxidation with oxygen of propenes deuteriated at the terminal carbon atoms [77]. The observed isotope effects proved to be greater than they should have been if the oxygen atom attacked directly the terminal carbon atom of the allyl radical, since in the latter case the question whether or not the attacked carbon atom contains H or D would have been insignificant.

The rate-limiting stage. On the basis of the kinetic data and the analogy between reactions (7), (11), and (12), it is assumed that dissociative adsorption of the olefinic hydrocarbons constitutes the slowest stage in these reactions. The zero order of reactions (7), (11), and (12) with respect to oxygen means that the rate of adsorption of oxygen at $P_{O_2} > (P_{O_2})_{min}$ is sufficiently high to compensate the time required for the conversion of the oxygen of the catalyst surface.

Thus in order to catalyse the allyl oxidation reaction, the catalyst must be capable of dissociating the C–H bond in the methyl group, while protecting at the same time the double bond in the initial olefin from oxidation. If the adsorption of the latter is so strong that it results in the dissociation of the double bond, degradative oxidation products are formed: acetaldehyde, formaldehyde, carbon dioxide, and others.

c. The Mechanism of the Oxidative Ammonolysis of Propenes

As stated above, the first stages of the oxidative ammonolysis and oxidation of propene to acrolein may be regarded as identical. According to Adams [77], the mechanism becomes different after the removal of the second hydrogen atom from the adsorbed hydrocarbon radical. In the presence of ammonium the unsaturated surface radical $L-\dot{C}H-CH=CH_2$ loses yet another hydrogen atom from the same carbon atom instead of combining with oxygen [reaction (20)]:

$$L_1-\dot{C}H-CH=CH_2 \xrightarrow{+L\dot{O}} L_1-\ddot{C}-CH=CH_2. \quad (21)$$

In turn the ammonia adsorbed in the presence of oxygen also undergoes oxidative dehydrogenation:

$$L_3(NH_3) + L-\dot{O} \rightarrow L_3(NH_2) + L-OH, \quad (22)$$

etc., until the formation of chemisorbed NH and N radicals, which is followed by the addition reaction, whose product is acrylonitrile:

$$L_1-\ddot{C}-CH=CH_2 + L_3-\ddot{N} \rightarrow CH_2-CH-CN + L_1 + L_3. \quad (23)$$

According to the views of Gel'bshtein and coworkers [78], acrylonitrile is formed consecutively via an intermediate stage in which acrolein is formed:

$$L_1(CH_2{=}CH{-}CHO) + L_3(NH) \rightarrow L_1(H_2C{=}CH{-}CN) + L_3(H_2O), \quad (24)$$

with subsequent desorption:

$$L_1(H_2C{=}CH{-}CN) \rightarrow L_1 + H_2C{=}CH{-}CN. \quad (25)$$

The kinetic equation derived on the hypothesis of the consecutive formation of acrylonitrile via acrolein as an intermediate [78] is qualitatively confirmed by experimental data. The formation of degradative reaction products (acetaldehyde, formaldehyde, hydrogen cyanide, acetonitrile, carbon dioxide, and others) may take place on catalytic centres where the adsorption of propene is stronger and is accompanied by the dissociation of the double bond.

d. The Mechanism of the Oxidative Dehydrogenation of Mono-olefins

In order to be capable of oxidative dehydrogenation to a diolefin, the initial olefin molecule must contain not less than four carbon atoms. By analogy with propene, the adsorption of n-butenes can be represented in the following manner:

$$\begin{matrix} CH_2{=}CH{-}CH_2{-}CH_3 \\ (\text{or } CH_3{-}CH{=}CH{-}CH_3) \end{matrix} \searrow \underbrace{H_2C \cdots CH \cdots CH}_{L_1}{-}CH_2 + \underset{L_2}{H}. \quad (26)$$

The C–H bonds at the secondary allyl carbon atom are more readily dissociated than those at the primary carbon atom, and therefore the dissociative adsorption of but-1-ene is faster than that of but-2-ene. In the oxidative dehydrogenation of n-butenes the second hydrogen atom is removed from the methyl group of the adsorbed hydrocarbon molecule and not from the allyl group as in the oxidation of propene to acrolein [Eqn. (17)] [77]:

$$\underbrace{H_2C \cdots CH \cdots CH}_{L_1}{-}CH_3 + \underset{L}{\dot{O}} \rightarrow \underbrace{H_2C \cdots CH \cdots CH}_{L_1}{-}\dot{C}H_2 + \underset{L}{OH}, \quad (27)$$

and further

$$\underbrace{H_2C \cdots CH \cdots CH}_{L_1}{-}\dot{C}H_2 \rightarrow L_1(H_2C{=}CH{-}CH{=}CH_2) \rightarrow L_1 + H_2C{=}CH{-}CH{=}CH_2. \quad (28)$$

The removal of a hydrogen atom from the methyl group probably takes place much more readily than its removal from the allyl group, i.e. the possibility of the formation of a conjugated diolefin is much greater than that of the formation of the corresponding aldehyde. Considerable amounts of aldehydes are formed only from olefins branched at the vinyl atom [69].

Apart from the formation of a diolefin or an aldehyde, there is also a possibility of the recombination of the allyl radical with a hydrogen atom initially removed from the mono-olefin molecule. In this case the initial olefin or one of its isomers (with respect to the double bond) is formed [Eqn. (26)]. However, isomerisation on catalysts such as bismuth molybdate takes place much more slowly than oxidative dehydrogenation.

As in the formation of unsaturated aldehydes and oxidative ammonolysis, the dissociative adsorption of the initial olefin must be adopted as the slowest stage in the oxidative dehydrogenation of mono-olefins to diolefins. Apart from the similarity of the kinetics of these three reactions, further evidence in favour of the above view comes also from the unequal reactivities of the individual n-butene isomers. The rate of oxidative dehydrogenation increases in the series *trans*-but-2-ene < *cis*-but-2-ene < but-1-ene, but, starting with the stage in which the adsorbed allyl radical is present, the individual n-butene isomers are no longer distinguishable [Eqn. (26)].

The rate of dissociative adsorption is determined by the stability of the C–H bond dissociated on formation of the allyl radical from the initial olefin molecule. In agreement with the energies required for the removal of the allyl hydrogen atom by radicals, the rate of oxidative dehydrogenation increases in the series primary > secondary > tertiary allyl hydrogen atoms in the mono-olefin molecule. An increase in rate in the above series is also observed in the formation of the allyl carbonium ion, in conformity with the available data[82], according to which the hydrocarbon radicals adsorbed on the surface of oxidation catalysts are positively charged.

e. Effect of the Nature of the Catalyst

At the present time differences in the catalytic activity of oxides due to their chemical nature are still little understood. The available literature data on the variation of the activity and selectivity of certain catalysts for oxidative dehydrogenation of olefins with the chemical composition were examined in section II, subsection 1. The relation between catalytic activity and catalyst composition in other oxidative reactions, in particular in the oxidation of propene to acrolein and oxidative ammonolysis, is described in Refs. 82–85, for example. Certain new results will be examined here.

Belen'kii and coworkers[86] compared the effects of the molybdenum : bismuth ratio on the catalytic activity in the oxidation of propene to acrolein and in the oxidative dehydrogenation of butenes and isopentenes. The optimum composition of the catalyst proved to be the same for all three reactions and corresponded to the atomic ratio Mo : Bi = 2. These results provide yet another confirmation of the validity of the hypotheses concerning the identity of the active centres of the catalysts in these reactions.

According to other data, the Mo : Bi atomic ratio in the most active catalysts varies between 1 and 2 and apparently depends on the method of preparation of the catalyst and the presence of other substances, in particular a carrier.

Several chemical compounds are formed in the system molybdenum–bismuth. The phase $Bi_2O_3.2MoO_3$, which corresponds to the atomic ratio Mo : Bi = 1, shows the highest activity, among the mixed oxides of molybdenum and bismuth, in the oxidation of propene to acrolein and oxidative ammonolysis to acrylonitrile[79,87,88] Bleijenberg et al.[89] did not observe the formation of the phase with the composition Mo : Bi = 1, and yet specimens with precisely this component ratio proved to be the most active in oxidative dehydrogenation[56]. The 1 : 1 atomic ratio corresponds also to the optimum composition of bismuth–tungsten catalysts[90], while in the best antimony–tin catalysts the atomic ratio is Sn : Sb = 1 : 8. The catalytic activities of various bismuth tungstates differ from one another less than those of bismuth molybdates. The most active form of the tungstate is in fact less active than that of bismuth molybdate.

There are as yet very few data concerning the nature of the active centres responsible for chemisorption and catalysis in the oxidative dehydrogenation of olefins. According to the views of Sachtler and De Boer[80], a bond between one of the carbon atoms and a surface oxygen atom forms in the dissociative adsorption of olefins on oxides. According to Trapnell[91], dissociative adsorption of hydrocarbons takes place on metal ions with an unfilled *d* shell. In the latter case two-point dissociative adsorption of the olefins can occur, for example at a doublet consisting of molybdenum and bismuth atoms. This hypothesis appears justified if it is remembered that catalysts with the atomic ratio Mo : Bi = 1 are active. The centre responsible for the dissociation of the double bond and degradative oxidation can have the same composition (a molybdenum or bismuth atom) but differs by the higher energy of the donor–acceptor interaction with the olefin molecule.

Stroeva and coworkers[92] investigated the relation between the composition of bismuth–molybdenum, cobalt–molybdenum, and antimony–tin catalysts and their electrical properties, on the one hand, and their activity in the oxidative oxidation of the C–H bond, on the other. If follows from the results that, for all three binary systems, the physicochemical nature of the promoting effect of the second oxide is different. In the system MoO_3–Bi_2O_3 the promoting effect is accompanied by the formation of a chemical compound with the atomic ratio Mo : Bi = 1. According to the above authors' views, the active centre is a doublet consisting of molybdenum and bismuth atoms. In the system MoO_3–Co_3O_4 the promoting effect of cobalt is associated with an increase of the specific surface: cobalt molybdate has no catalytic properties and behaves as a carrier. The active centre can consist of two molybdenum atoms. In the system Sb_2O_4–SnO_2 the possible role of tin consists in an increase of the concentration of antimony cations in the most oxidised state and also in an increase of the internal surface of the catalyst. The active centre can consist of two antimony atoms.

Batist et al.[56] suggest that the formation of the intermediate allyl structure on the surface of the bismuth–molybdenum catalyst occurs at the vacant anionic site which is produced as a result of the removal from the surface of the hydroxyls formed in selective oxidation reactions [reactions (17), (21), and others]:

$$2\,OH^- \rightarrow H_2O + \square_d + O^{-2}, \qquad (29)$$

where $\square_d$ is a vacant anionic site. The adsorbed allyl radical is bound to a molybdenum ion via a π-bond. According to Batist et al.[56], the promoting effect of bismuth is associated with an increase in the susceptibility of the catalyst to dehydroxylation and reduction.

In a number of studies attempts were made to establish correlations between the catalytic and other physicochemical properties of the catalysts associated with the mobility of their ions and electrons. Sachtler and De Boer[80] compared the activities, selectivities, and capacities for reduction of the catalysts, and Gel'bshtein, Margolis, and coworkers[78,87,80] compared the catalytic properties and electron work functions.

According to the data of Kolchin et al.[87], the maximum electron work function of mixed bismuth and molybdenum oxides is observed at an atomic ratio of 6 : 4, i.e. corresponds approximately to the highest activity of the catalyst. However, according to other data[78], there is no parallel variation of the electron work function and catalytic activity of the oxidation of propene to acrolein and oxidative ammonolysis. Kolchin et al.[90] arrived at the same conclusion in a similar study of bismuth–tungsten catalysts.

According to the data of Sachtler and De Boer[80], the conversion of propene and the selectivity with respect to acrolein are roughly correlated with the susceptibility of the catalysts to reduction. The susceptibility to reduction (Table 3) was defined as the reciprocal of the absolute temperature at which a rate of reduction of 7.4×10^{-3} moles of hydrogen per gramme of catalyst per hour ($T_{7.4}$) is attained. Under the conditions of the experiments, the principal oxidation products were acrolein, carbon monoxide, and carbon dioxide. With increase in the susceptibility of the catalysts to reduction, the overall degree of conversion of

propene increases and the selectivity with respect to acrolein falls.

The existence of a relation between catalytic activity and the susceptibility of the catalyst to reduction may be attributed to the fact that the susceptibility of the oxide to reduction reflects the mobility of its constituent oxygen, which participates in the catalytic steps in the oxidation of propene. Low mobility is the reason for low activity of the catalyst. On the other hand, if the mobility of oxygen is too high, the formation of the products of the total oxidation of the hydrocarbon is facilitated: for selective oxidation of the C–H bond, the mobility of oxygen should have a definite optimum value.

Table 3. Dependence of the degree of oxidation of propene on the susceptibility of the catalyst to reduction.

Metal of the oxide	Susceptibility to reduction $10^3/T_{7.4}$, deg^{-1}	Yields of propene oxidation products at 520°C, %		
		overall conversion	acrolein	selectivity with respect to acrolein
Mo deposited at 98°C	1.17	2	2	70
Mo deposited at 20°C	1.29	16	9	59
Mo–Bi	1.51	66	55	84
W–Bi	1.52	55	32	58
Mo–Co	1.54	28	9	32
Sn–Sb–Mo	1.70	29	13	46
Mo–Cu	1.73	55	28	50
Mn	2.02	~100	~0	~0

Sachtler and De Boer[80] obtained a kinetic equation based on the theory of absolute reaction rates with the following main assumptions: (a) carbon and oxygen compete in the adsorption process; (b) the rate of adsorption of oxygen greatly exceeds the rate of its consumption by reaction (11); (c) carbon dioxide and carbon monoxide are formed from acrolein. This kinetic equation is qualitatively consistent with the experimental observation that the activity and the selectivity vary with the susceptibility of the catalyst to reduction.

III. OXIDATIVE DEHYDROGENATION OF SATURATED HYDROCARBONS

In contrast to mono-olefins, the oxidation of saturated hydrocarbons with oxygen gives low yields of dehydrogenation products. Therefore much attention has been given to oxidative dehydrogenation under the action of reagents more effective than oxygen, in the first place iodine. When iodine was applied, fairly high yields were obtained and fairly high selectivity with respect to the dehydrogenation products was achieved.

We shall examine initially oxidative dehydrogenation with oxygen.

1. DEHYDROGENATION IN THE PRESENCE OF OXYGEN

The dehydrogenation of saturated hydrocarbons in the presence of oxygen, like that of olefins, in an oxidative, and not a dehydrogenation, reaction accompanied by subsequent oxidation of hydrogen. Depending on the experimental conditions, different proportions of oxygen-containing compounds and cracking products are formed together with the dehydrogenation products. Oxidation reactions are of the radical-chain type and take place mainly in the bulk-phase of the reaction system. In contrast to olefins, solid catalysts which have an effective selective dehydrogenating effect in the oxidative dehydrogenation of saturated hydrocarbons are unknown. The catalysts used were capable only of a comparatively slight increase in the yield of the dehydrogenation products.

a. Low- and High-Temperature Oxidation of Hydrocarbons

Most hydrocarbons are oxidised at about 300°C and below, and in many respects the mechanism of this oxidation is radically different from the mechanism of oxidation at higher temperatures. The products of the low-temperature oxidation of hydrocarbons are mainly aldehydes, ketones, alcohols, carbon monoxide, and carbon dioxide; in the high-temperature oxidation the principal reactions are cracking and dehydrogenation. Under the conditions usually employed, the transition from the low- to the high-temperature mechanism usually occurs in the range 350–500°C. This range depends relatively little on the individual hydrocarbon, so that the oxidations of many saturated hydrocarbons probably occur by similar mechanisms. In the temperature range for the transition from one mechanism to the other the temperature coefficient of the rate of oxidation is anomalous: with increase in temperature, the rate of reaction passes through a minimum in the transition region.

There are numerous data[93–107] concerning the amounts of unsaturated hydrocarbons formed as a function of the experimental conditions. Some of these are quoted in Table 4. With increase in the butane oxidation temperature from 300° to 700°C, the yield of oxygen-containing compounds decreases, that of ethylene and propene increases, and that of butenes passes through a maximum[107]. The extent of formation of oxygen-containing organic products also falls markedly as the oxygen : carbon ratio decreases. For example, with the ratio oxygen : butane ≤ 0.1, at 500°C virtually the only oxygen-containing compound is water[103]. In the homogeneous oxidation of saturated hydrocarbons small amounts of diolefins sometimes form in addition to mono-olefins[104] and in the high-temperature oxidation of ethane small amounts of acetylene are produced[98].

The yields of diolefins obtained were not limited by the equilibrium: the equilibrium yields of diolefins in the oxidation of saturated hydrocarbon by oxygen at about 500°C, at atmospheric pressure, and with the equivalent composition of the initial mixture can reach 100%.[108]

b. The Mechanism of the High-Temperature Oxidation

The mechanism of the formation of olefins under the conditions of the homogeneous oxidation of saturated hydrocarbons has been the subject of discussion for a long time. The mechanism proposed by Shtern[95] for the oxidation of propane may be regarded as one of the most successful mechanisms for the oxidation of saturated hydrocarbons available at present. According to this mechanism, propene forms as a result of the removal by an oxygen molecule of a hydrogen atom from the propane and the subsequent breakdown of the resulting propyl radical into propene and a hydrogen atom:

$$C_3H_8 + O_2 \rightarrow \text{iso-}\dot{C}_3H_7 + H\dot{O}_2, \qquad (30)$$

$$\text{iso-}\dot{C}_3H_7 \rightarrow C_3H_6 + \dot{H}. \quad (31)$$

Nevertheless this reaction path appears unlikely because of the high activation energy (about 40 kcal mole^{-1}) of stage (31). Therefore Semenov [109] suggested the following mechanism for the conversion of propane into propene:

$$C_3H_8 + O_2 \rightarrow \text{iso-}C_3H_7 + H\dot{O}_2, \quad (32)$$

$$\text{iso-}\dot{C}_3H_7 + O_2 \rightarrow CH_3{-}\underset{\dot{O}{-}O}{CH}{-}CH_3. \quad (33)$$

After isomerisation the peroxy-radical formed breaks down with formation of propene:

$$CH_3{-}\underset{\dot{O}{-}O}{CH}{-}CH_3 \rightarrow CH_3{-}\underset{\dot{O}{-}OH}{CH}{-}\dot{C}H_2, \quad (34)$$

$$CH_3{-}\underset{\dot{O}{-}OH}{CH}{-}\dot{C}H_2 \rightarrow C_3H_6 + H\dot{O}_2. \quad (35)$$

However this mechanism too met with objections [95], since it leads to a no less serious inconsistency with experiment. In particular the ratio of the rates of formation of organic products with and without oxygen should have been much greater than is found experimentally [95].

Table 4. Formation of olefins in the oxidation of certain saturated hydrocarbons.

Initial hydrocarbon	Moles of oxygen per mole of hydrocarbon in the starting material	Temperature, °C	Pressure, atm	Dehydrogenation to mono-olefins, %		References
				with respect to starting material	with respect to product	
Ethane	0.3	680	1	50	62	101
Propane	0.23	700	1	15	25	101
Propane	0.17	540	1	16	56	102
Propane	0.5	465	0.4	20	49	95
Propane	1	350	0.4	13	25	95
n-Butane	0.1	500	0.55	7	35	103
n-Pentane	1	500	1	10	25	104
Isopentane	0.5	400	1	9	30	105
Cyclohexane	2.7	400	1	15*		106

* Yield of cyclohexene

The majority of present day investigators assume that the second stage of the reaction involves the removal by an oxygen molecule of a hydrogen atom from the alkyl radical [103-105,110-112]:

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + H\dot{O}_2. \quad (36)$$

Appleby and coworkers [103] obtained the following equation for the reaction of n-butane at low oxygen : butane ratios:

$$-\frac{d[C_4H_{10}]}{d\tau} = k[C_4H_{10}]^{3/2}[O_2]^{1/2}. \quad (37)$$

The kinetic data were obtained by a flow method at 485-525°C (τ is the contact time): Eqn. (37) was derived by the stationary-state method using the following mechanism:

$$C_4H_{10} + O_2 \rightarrow C_4H_9 + HO_2, \quad (38)$$

$$C_4H_9 + O_2 \rightarrow C_4H_8 + HO_2, \quad (39)$$

$$HO_2 + C_4H_{10} \rightarrow H_2O_2 + C_4H_9, \quad (40)$$

$$2HO_2 \rightarrow H_2O_2 + O_2, \quad (41)$$

$$H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2, \quad (42)$$

$$2HO_2 \xrightarrow{\text{wall}} H_2O + 1\,{}^1/_2O_2, \quad (43)$$

$$C_4H_9 \rightarrow CH_3 + C_3H_6, \quad (44)$$

$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9, \quad (45)$$

$$C_4H_9 \rightarrow C_2H_5 + C_2H_4, \quad (46)$$

$$C_2H_5 + C_4H_{10} \rightarrow C_2H_6 + C_4H_9. \quad (47)$$

c. Effect of the Solid Surface

Eqns. (38)-(47) show that the above mechanism of oxidative dehydrogenation and cracking presupposes chain termination on the walls. In actual fact, however, in hydrocarbon oxidation reactions both chain initiation and chain termination probably occur on the walls of the reactor. The available experimental literature data on the effect of the wall on the reaction of saturated hydrocarbons in the presence of oxygen are extremely few and non-systematic. However, it is possible to arrive at the reliable conclusion, on their basis, that the surface of the wall does indeed influence the reaction and that, depending on the experimental conditions and the nature of the wall, the latter can both slow down and accelerate the reaction. The initiating effect of the surface can be associated, for example, with the fact that it facilitates the removal of a hydrogen atom from the hydrocarbon molecule as a result of the chemisorption of oxygen:

$$L - \dot{O}_2 + C_4H_{10} \rightarrow L{-}O_2H + \dot{C}_4H_9, \quad (48)$$

$$L - \dot{O}_2 + \dot{C}_4H_9 \rightarrow L - O_2H + C_4H_8, \quad (49)$$

The possible mechanism of the further conversion of the mono-olefin into the diolefin was examined in section II, subsection 3d.

Martin and Niclause [113,114] investigated the effect of the reactor walls on the pyrolysis of propane and isopentane in the presence of added oxygen (up to 2%). The experiments were performed in a static reactor at initial hydrocarbon pressures of 25-50 mmHg at 480-550°C. The pyrolysis of propane takes place with formation of the following main products: propene, ethylene, methane, and hydrogen. In the pyrolysis of isopentane cracking products are mainly formed. When the surface : volume ratio ($S:V$) for the reactor is increased, the rate of reaction falls, which suggests that the walls of the Pyrex reactor have an inhibiting effect. The pyrolysis was accelerated by washing the reactor with the chromic acid mixture and by preliminary treatment with steam but was retarded when the walls were covered with potassium chloride or lead oxide (PbO).

Selwitz and Stanmyer [105] compared the conversion of isopentane into isopentenes at 400°C in reactors made of quartz, stainless steel, and quartz covered by a thin layer of silver. The smallest yield of isopentene was observed in the reactor whose walls had been covered by a layer of silver, and, what is more, the latter was markedly corroded during the reaction.

According to the data of Sultanova and Nagiev [115], quartz packing somewhat accelerates the dehydrogenation of diethylbenzenes to divinylbenzenes in the presence of hydrogen peroxide, which is decomposed under the conditions of the reaction with formation of oxygen. The favourable effect of the quartz surface on the dehydrogenation is also stated in a patent [116], where it is recommended that n-butene be brought into contact with alternating layers of activated charcoal and quartz. Although only about 8% of the hydrocarbon is then converted into n-butenes, fairly high selectivity (64%) is attained.

Various investigators attempted to increase the yields of the products of oxidative dehydrogenation by using other solid catalysts. Vanadium oxide "or its mixtures with oxides of tin, cobalt, chromium, manganese, uranium, tungsten, lead, bismuth, or zinc" have been suggested as catalysts in certain patents [117,118]. Under optimum conditions (temperature 400°C, n-butane : O_2 : diluent = 1 : 1 : 9) about 10% of butenes and only 1.9% of divinyl is obtained. However, the selectivity with respect to olefins is about 85%. Some patents [119,120] recommend calcium and nickel phosphates, on which yields of 6% of divinyl and 2% of butenes were attained. Ferric, manganic, or germanium oxides and calcium or lithium chlorides have been recommended as catalysts for the oxidative dehydrogenation of saturated hydrocarbons in the presence of oxygen [121].

The authors of some patents [122,123] assert that 17% of the initial n-butane is converted into divinyl in the course of 100 min on a fluidised bed of sodium phosphomolybdate with discontinuous contact. The formation of such large amounts of diolefins is probably related less to the nature of the catalyst than to reactor design or other factors which influence the process.

It follows from the data examined that in most cases the yields of olefins obtained on solid catalysts are close to those in an empty reactor (Table 4), but the selectivity in the presence of a solid catalyst is much higher. This suggests that the role of the solid catalyst may consist in the suppression of side-reactions. This may apply primarily to cracking reactions.

d. Effect of Radical-Forming Additives

The oxidative dehydrogenation of saturated paraffins, like that of olefins, can be greatly accelerated under the influence of small amounts of certain additives, which readily give rise to free radicals. Thus, on addition of iodine to a reaction mixture containing a saturated hydrocarbon and oxygen, the yields of dehydrogenation products increase sharply [108,124-126]. Apart from iodine, oxidative dehydrogenation by oxygen is activated also by other halogens or substances which decompose with formation of halogens: hydrogen and ammonium halides [127] and alkyl halides [128]; or the reaction can be activated by passing the reaction mixture through fused halides, for example lithium, lead, cadmium, etc. iodides [129-131].

The addition of ozone at temperatures in excess of 400°C also accelerates the yields of saturated hydrocarbon dehydrogenation products [105]; on the other hand, at lower temperatures ozone retards the dehydrogenation. Added butenes also have an inhibiting effect on the dehydrogenation of butane [76,103]. The oxidative dehydrogenation of saturated hydrocarbons in the presence of oxygen and small amounts of radical-generating substances will be examined in detail in subsection 3.

2. DEHYDROGENATION IN THE PRESENCE OF IODINE

The method of oxidative dehydrogenation with iodine was proposed in a number of patents, mainly in 1958–1959. [30,132]

a. Dehydrogenation Without an Acceptor and Oxygen

Raley and coworkers [133] investigated the reaction of iodine with saturated hydrocarbons ranging from C_2 to C_5, cyclopentane, and methylcyclopentane at temperatures between 495° and 685°C, iodine : hydrocarbon molar ratios between 0.4 and 4.6, and various contact times. Under these conditions the principal reactions involved dehydrogenation:

$$C_nH_{2n+2} + 2I_2 \rightleftarrows C_nH_{2n-2} + 4HI, \quad (3)$$

$$C_nH_{2n+2} + I_2 \rightleftarrows C_nH_{2n} + 2HI, \quad (50)$$

and

$$C_nH_{2n} + I_2 \rightleftarrows C_nH_{2n-2} + 2HI. \quad (51)$$

Hydrogen iodide is formed in an amount which is almost equivalent to the iodine which has reacted. Organic iodides and polymers were observed as side-products.

The equilibrium yields of propane and isobutane dehydrogenation products in the reaction with iodine are quoted by Benson and coworkers [134,135] and those for n-butane by Kozorezov [136] and Basner et al. [137]. When the temperature is raised above approximately 450°C, the diolefins : mono-olefins ratio increases appreciably, but below 600°C mono-olefins predominate. As the contact time is increased until equilibrium is attained, the yields of dehydrogenation products also increase, while the diolefins to mono-olefins ratio falls (Table 5). [133]

Table 5. Effect of the duration of contact at 550°C.

Reactants	Iodine : n-butane = 1.3			Iodine : isopentane = 1.6		
Duration of contact, s	0.7	1.3	equilibrium	1.3	2.6	equilibrium
Degree of conversion of C_nH_{2n+2}, %	51	76	82	69	90	92
C_nH_{2n-2}/C_nH_{2n}	0.38	0.28	0.24	0.42	0.28	0.27
Yield of C_nH_{2n-2}, %	14	16	16	19	18	20

If the initial saturated hydrocarbon contains six and more carbon atoms in its chain, aromatic hydrocarbons are formed together with olefins [138-140]:

$$C_nH_{2n-2} + I_2 \rightleftarrows C_nH_{2n-4} + 2HI \quad (52)$$

and

$$C_nH_{2n-4} + I_2 \rightleftarrows C_nH_{2n-6} + 2HI \quad (53)$$

(for $n \geqslant 6$). With increase of the iodine : hexane ratio from 0 to 2 at 500°C the degree of conversion into dehydrocyclisation products increases [138]. At low iodine : hexane ratios (up to 0.1–0.15) the dominant products are hydrocarbons with five or less carbon atoms. The same dehydrogenation products as in the reaction of saturated hydrocarbons with iodine (mono- and di-olefins, aromatic compounds, and others) can be obtained when iodine is replaced by bromine [141].

b. Kinetics of the Dehydrogenation Reaction

Teranishi and Benson [142] investigated the kinetics of the dehydrogenation of isobutane with iodine in a static reactor at 250–310°C. No induction period was observed. The reaction kinetics are described by the equation

$$\frac{[\text{iso-}C_4H_{10}](1-B)}{2S} = a_1 + a_2\frac{[HI]}{[I_2]^{1/2}} + b\frac{[HI]}{[I_2]}, \quad (54)$$

where $B = [\text{iso-}C_4H_8][HI]^2/K[\text{iso-}C_4H_{10}][I_2]$ and K is the equilibrium constant for the overall reaction

$$\text{iso-}C_4H_{10} + I_2 \rightleftarrows \text{iso-}C_4H_8 + 2HI, \quad (55)$$

$S = -d[I_2]^{1/2}/dt$ and a_1, a_2, and b are constants. An equation similar to Eqn. (54) also describes the kinetics of the dehydrogenation of propane with iodine [143].

c. The Mechanism of the Dehydrogenation Reaction

The dissociation energy of the iodine molecule is low (36 kcal mole^{-1}) and at high temperatures iodine breaks down partially into atoms:

$$I_2 + M \rightleftarrows 2\dot{I} + M. \quad (56)$$

In the reaction with a saturated hydrocarbon molecule the iodine atom abstracts a hydrogen atom, yielding an alkyl radical:

$$n\text{-}C_4H_{10} + \dot{I} \rightleftarrows HI + n\text{-}\dot{C}_4H_9. \quad (57)$$

Depending on the conditions, the alkyl radical undergoes different further reactions. At temperatures up to 500°C and above cracking occurs predominantly in the presence of low iodine concentrations:

$$n\text{-}\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4, \quad (58)$$

while at higher iodine concentrations butenes are mainly formed:

$$\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI. \quad (59)$$

At temperatures much lower than 500°C the amount of dissociated iodine is small and butenes can be produced via the intermediate formation of iodides, for example [133]:

$$\dot{C}_4H_9 + I_2 \rightarrow C_4H_9I + \dot{I}, \quad (60)$$

$$C_4H_9I + \dot{I} \rightarrow \dot{C}_4H_8I + HI, \quad (61)$$

$$\dot{C}_4H_8I \rightleftarrows C_4H_8 + \dot{I}. \quad (62)$$

The kinetic data of Benson and coworkers [142,143] are consistent with the hypothesis that the slowest stage of the reaction is the removal of a hydrogen atom from the saturated hydrocarbon molecule:

$$\dot{I} + RH \rightleftarrows \dot{R} + HI. \quad (63)$$

Eqn. (54), which describes satisfactorily the experimental data for the dehydrogenation of propane and isobutane by iodine, was obtained on the assumption of a steady state for the alkyl radical and alkyl iodide.

According to Raley et al. [133], the conversion of mono-olefins into diolefins is similar to the conversion of saturated hydrocarbons into mono-olefins. The rate of the mono-olefins → diolefins reaction is much higher than that of the saturated hydrocarbons → mono-olefins reaction and the equilibrium yields of diolefins at temperatures of the order of 500°C are lower than those of mono-olefins. This can explain the experimental finding that the diolefins to mono-olefins ratio decreases as the system approaches equilibrium (Table 5).

According to the data of Back and Cvetanovich [144] the conversion of but-1-ene into divinyl at 65°C in the presence of iodine can occur with intermediate formation of iodides and iodine-containing radicals:

$$\dot{I} + C_4H_8 \rightarrow C_4H_8I. \quad (64)$$

C_4H_8I is a radical or π-complex from which a hydrogen atom is removed:

$$C_4H_8I + \dot{I} \rightarrow C_4H_7I + HI. \quad (65)$$

Then follows the rapid stage

$$C_4H_7I + \dot{I} \rightarrow \dot{C}_4H_7I_2, \quad (66)$$

and subsequently

$$\dot{C}_4H_7I_2 + \dot{I} \rightarrow C_4H_6I_2 + HI, \quad (67)$$

$$C_4H_6I_2 \rightarrow C_4H_6 + I_2. \quad (68)$$

Thus according to modern theories, the high-temperature conversion of saturated hydrocarbons into diolefins in the presence of iodine involves a chain mechanism with intermediate formation of hydrocarbon radicals and mono-olefins. The rate of conversion of mono-olefins into diolefins is much higher than that of saturated hydrocarbons into mono-olefins. At lower temperatures there is also the possibility of the intermediate formation of iodides and iodide radicals.

d. Dehydrogenation in the Presence of Acceptors and Solid Catalysts

The iodine which has reacted can be regenerated by means of solid acceptors in accordance with Eqns. (5) and (6). If an acceptor is introduced into the reaction zone, then, as a result of the adsorption of hydrogen iodide, the equilibria of reactions (3) and (51) are displaced towards the formation of diolefins which leads to an appreciable increase in their yields.

The dehydrogenation of n-butane by iodine in a flow reactor at 520–524°C using butane diluted with nitrogen in the proportions butane : nitrogen = 1, in the presence of manganese dioxide as an acceptor, was investigated by Kolobikhin and coworkers [145]. Apart from divinyl and n-butene, cracking products, organoiodine compounds, and resinous and solid products were observed. Hydrogen and isomerisation products do not form in appreciable amounts. As the iodine : butane ratio is increased from zero to 1.43, the yields of divinyl likewise increase and those of butenes and cracking products pass through a maximum. On further dilution with nitrogen from 1 : 1 to 1 : 4, the yields of divinyl change slightly but those of butenes decrease appreciably [146].

The productivity of apparatus for oxidative dehydrogenation with iodine can be enhanced by using reactors with a fluidised acceptor bed [147]. Here the spent acceptor is continuously removed from the reaction zone. On raising the temperature from 480° to 580°C in apparatus with a fluidised acceptor bed the degree of conversion of n-butane increased and the maximum selectivity with respect to dehydrogenation products was observed at 550°C. An increase of the contact time above the optimum value favours cracking and complete oxidation of hydrocarbons by the oxygen of the acceptor.

The dehydrogenation of isopentane in the presence of iodine and manganese oxides shows approximately the same features as the dehydrogenation of n-butane [148].

An increase in the yields of the dehydrogenation products in the presence of iodine can also be achieved by the introduction of solid catalysts which do not behave as acceptors of hydrogen iodide (platinum, palladium, ferrous iodide, cupric iodide, and others) [138,149], whose activity is attributed to their capacity to catalyse the decomposition of hydrogen iodide:

$$HI \rightarrow H_2 + I_2, \quad (69)$$

e. Dehydrogenation in the Presence of Oxygen

Introduction of oxygen into a reaction system containing a saturated hydrocarbon and iodine leads to an appreciable

increase of the yield of diolefins [133,145,148,150,151]. Oxygen-containing organic products are then formed only in small amounts. If oxygen is present in the system, a smaller amount of iodine is required for the attainment of the same yield of divinyl.

The accelerating effect of oxygen on the formation of diolefins is associated primarily with the oxidation of hydrogen iodide by reaction (4), which leads to the regeneration of iodine. There are reasons to believe that the role of oxygen is not restricted to the oxidation of hydrogen iodide. This problem will be discussed in greater detail in subsection 3.

f. Chemical Composition and the Porous Structure of the Acceptor

Apart from manganese oxides, mixtures of iron oxide with potassium iodide [152] and of manganese and calcium oxides [153], nickel oxide [154], copper [155], etc. have been proposed as hydrogen iodide acceptors. The oxides, hydroxides, or carbonates of various metals can also serve as acceptors of hydrogen bromide if bromine is used instead of iodine in the oxidative dehydrogenation [156].

Tyuryaev and coworkers [157,158] made a comparative study of various acceptors. Among the acceptors tested—the oxides of calcium, barium, strontium, zinc, nickel, iron, cobalt, copper, and manganese—the highest yields of isoprene were obtained on barium, calcium, and manganese oxides. Among metal carbonates, the most effective absorbers of hydrogen iodide are sodium and barium carbonates. The manganese oxide giving the highest yield of isoprene is Mn_3O_4. However, on repeated use, all the oxides tested (Mn_2O_3, MnO_2, and Mn_3O_4) exhibit approximately the same properties in the dehydrogenation processes [148]. This is because the reaction of hydrogen iodide with the oxides results, regardless of the composition of the latter, in the formation of manganese(II) iodide, which yields Mn_3O_4 in the regeneration process under the influence of oxygen:

$$3\,MnI_2 + 2O_2 \rightarrow Mn_3O_4 + 3\,I_2. \qquad (70)$$

Calcium oxide is a more active acceptor than calcium carbonate [159]. When the experiments are repeated on any of the above acceptors, the composition of the latter changes to the steady-state composition corresponding to the ratio $CaO : CaCO_3 = 1 : 3-4$ (by weight).

There is a simple relation between the nature of the oxide and the acceptor capacity: the yields of isoprene vary in parallel with the decrease of the free energy of the reaction in which the acceptor combines with hydrogen iodide [157].

Metal oxide acceptors can be prepared by impregnating porous carriers [150,151,153,160]. Kolobikhin and coworkers [160] compared the following materials as carriers for manganese oxides: KSM and steam-treated silica gels, aluminosilicate, and γ-alumina. The yields of divinyl and the selectivity fall with decrease in pore size and with increase of the specific surface, and they depend on the nature of the carrier. Under the experimental conditions [160] the test specimens were regenerated at different rates and the degree of regeneration was not the same. Therefore the reduction of divinyl yields observed on decrease of acceptor pore size can be the result of the overall effect of two factors: incomplete regeneration of the acceptor and decrease of the rate of absorption of hydrogen iodide by the acceptor. Both phenomena may be associated with an increase of inhibition of the process by factors dependent on internal diffusion.

The present author [161] compared the effects of two acceptor specimens: one porous and one with low porosity. The first consisted of calcium oxide deposited on KSK silica gel and the second was obtained by mixing calcium oxide with a small amount of kaolin (Table 6). Whereas high yields of divinyl were obtained on both specimens, very little isoprene was produced in the presence of the porous specimen. It is difficult to explain by internal-diffusion-dependent factors such striking difference in the behaviour of n-butane and isopentane on changing the porous structure of the catalyst, in view of the slight difference in the dimensions of the n-butane and isopentane molecules compared with the dimensions of the pores of the coarsely porous silica gel. We shall return to this problem later.

Table 6. Effect of the porosity of the acceptor on the oxidative dehydrogenation of saturated hydrocarbons.

Catalyst	Specific surface, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Hydrocarbon	Yields under optimum conditions, %	
				of di-olefins*	of mono-olefins*
CaO with added kaolin	0.7	0.05	n-butane	69	<1
			isopentane	41	<1
CaO on KSK silica gel	100	0.4	n-butane	67	8
			isopentane	1	26

* With the same number of carbon atoms as the initial saturated hydrocarbon.

3. DEHYDROGENATION IN THE PRESENCE OF OXYGEN AND SMALL AMOUNTS OF IODINE

a. Some Experimental Data

The effect of oxygen on the oxidative dehydrogenation of saturated hydrocarbons in the presence of nearly equivalent amounts of iodine was examined in subsection 2e. Here we shall examine the features of the process in the presence of small amounts of iodine, sufficient only for the initiation or inhibition of reaction. As will be seen below, under these conditions the dehydrogenation reaction has certain specific features.

The variation of the degree of conversion of n-butane with temperature, duration of contact, and the concentrations of iodine and oxygen was investigated by Kuz'michev et al. [108]. The maximum yields of divinyl were obtained at 530°C. At higher temperatures the yields of cracking and combustion products increase and there is more coke formation. In the absence of iodine the main reaction is oxidative cracking†. On addition of small amounts of iodine, the cracking and overall conversion curves pass through a minimum. A sharp increase in the yield of divinyl is observed on raising the iodine : n-butane ratio to 0.05–0.06. On further increase of the concentration of iodine, the change in the yield of divinyl is less pronounced, while the yield of butenes continuously increases. The addition of small amounts of oxygen accelerates mainly the cracking reaction. A considerable increase in the yield of divinyl is observed only for oxygen : n-butane ratios in excess of 0.5.

† Cracking is the main reaction also at much lower temperatures [108].

Adel'son and Nikonov [162,163] did not observe a minimum on the curve relating the degree of conversion to the concentration of iodine in the dehydrogenation of isopentane. The present author investigated [164] the comparative effects of the addition of iodine and hydrogen iodide and bromide on the reaction of n-butane in the presence of oxygen. It was shown that, with the same amount of added halogen, the yields of divinyl decrease in the series HI > I_2 > HBr.

b. The Possible Mechanism of Dehydrogenation in the Presence of Added Halogen

When the hydrocarbon, iodine, and oxygen are present simultaneously, the reaction of the hydrocarbon with iodine takes place more readily than with oxygen. Therefore, according to the existing hypotheses [125,133,165], oxidative dehydrogenation in the presence of both oxygen and iodine has the same mechanism as without oxygen (see subsection 2c), the role of oxygen consisting in regeneration by reaction (4). However, it is quite likely that its role is not limited to interaction with hydrogen iodide but that oxygen participates actively in the intermediate stages of the formation of dehydrogenation products. Then in the presence of equivalent proportions of oxygen and the saturated hydrocarbon small amounts of added iodine can be regarded as reaction initiators. Iodine is known to initiate certain hydrocarbon oxidation reactions at high temperatures [95].

With equivalent proportions of the hydrocarbon and oxygen in the absence of iodine, the main reaction is cracking. The minimum in the degree of conversion at iodine : n-butane ratios between 0.01 and 0.02 can be accounted for by the dual function of iodine: inhibition of the cracking reaction and participation in oxidative dehydrogenation. If the role of iodine was restricted to the initiation of the reaction between the saturated hydrocarbon and oxygen, the addition of iodine would not significantly alter the relative yields of various products but the overall conversion would then certainly be increased. If the role of iodine consisted only in the inhibition of cracking, then, after a decrease in the rate of the latter to a minimum, further addition would not increase the yield of dehydrogenation products. Probably in oxidative cracking unstable intermediate compounds are formed, which are the first to be attacked by the added iodine. On increasing the amount of iodine, the latter acts in addition as a reactant in oxidative dehydrogenation.

At a low iodine concentration the variation of the yield of divinyl with the concentration of oxygen consists of two steps: a significant increase in the yield of divinyl is observed at oxygen : n-butane ratios ranging approximately from zero to 0.1 and from 0.55 to 0.8. It is difficult to explain the second rise in the divinyl yield curve (at high oxygen concentrations) from the standpoint that the role of oxygen is limited to oxidation of the hydrogen iodide produced, since oxygen is in considerable excess relative to the hydrogen iodide present. There are also other grounds to believe that the role of oxygen is not restricted to oxidation of hydrogen iodide. Thus, according to the data obtained by the present author, the introduction of oxygen favours the decomposition of iodine-containing hydrocarbon derivatives into unsaturated compounds. Therefore, apart from the cracking reaction, the role of oxygen consists also in participation in dehydrogenation by oxidising hydrogen iodide and probably in interaction with hydrocarbon molecules or intermediate iodine-containing species.

To investigate the kinetics of dehydrogenation in the presence of added iodine, the present author [166] used a reactor with internal stirring. The order of the divinyl formation reaction and of the overall reaction proved to be 0.4–0.55. This suggests that a hydrocarbon molecule or a hydrocarbon radical participates in the slowest stage and therefore the rate-limiting stage is not the dissociation of iodine [reaction (56)] or oxidation of hydrogen iodide [reaction (4)]. It was also shown that the oxidation of hydrogen iodide is faster than oxidative dehydrogenation [164].

Since reaction (4) is fast, when added iodine is replaced by hydrogen iodide, the reaction system contains almost the same quantity of molecular iodine as when the latter is added directly into the reactor. However, in the presence of hydrogen iodide there is the additional possibility [apart from the dissociation of iodine molecules by reaction (56)] that iodine atoms and also HO_2 radicals will enter the system:

$$HI + O_2 \rightarrow \dot{I} + H\dot{O}_2. \qquad (71)$$

Therefore the yields of divinyl in the presence of hydrogen iodide are higher than with the same amounts of iodine. When iodine is replaced by bromine, the rate of dehydrogenation decreases appreciably because of the higher dissociation energy of the Br–Br bond (46 kcal $mole^{-1}$) compared with the dissociation energy of the I–I bond (36 kcal $mole^{-1}$).

c. Effect of a Solid Surface on Dehydrogenation in the Presence of Oxygen and Added Iodine

When the walls of the quartz reactor are lined with sodium chloride or alumina or a steel reactor is used, the yields of divinyl are appreciably reduced [167]. In order to determine whether the observed effect is due to the inhibiting effect of alumina and sodium chloride or whether, on the other hand, it is caused by the activation of dehydrogenation by the quartz surface, the effect of the volume to surface ratio for the reactor on the degree of conversion of n-butane was investigated. The results show that the walls of the quartz (and also Pyrex) reactor appreciably accelerate the dehydrogenation. For example, when the volume : surface ratio of a quartz reactor was increased from 0.015 to 0.34 cm, the yield of divinyl decreased from 18 to 9%.

The comparative effects of certain solid catalysts on the yields of dehydrogenation products are shown in Table 7. [161,167] Depending on its nature and porous structure, the catalyst accelerates or inhibits the dehydrogenation reaction. The yields of divinyl on silica gel with a specific surface of 24 $m^2 g^{-1}$ are much higher than on quartz. However, on increasing the specific surface to 120 $m^2 g^{-1}$, the efficiency of the process is somewhat reduced. On alumina the yields of divinyl fall appreciably on increasing the specific surface of the catalyst. Other relations are observed for isopentane and n-hexane. The maximum yields of isoprene are obtained on non-porous catalysts, in agreement also with data on the effect of the porosity of the acceptors (Table 6). On the other hand, even alumina with the highest specific surface has a favourable effect on the dehydrocyclisation of n-hexane.

Apart from the substances listed in Table 7, other active catalysts have been proposed for the dehydrogenation of saturated hydrocarbons in the presence of added iodine: halides of alkali and transition metals and silver on silica gel or α-alumina [168–172], Fe_3O_4, and lithium hydroxide [173].

d. Possible Role of the Solid Catalyst

Since, as in the absence of iodine (subsection 1c), it is unlikely that the acceleration of dehydrogenation in the presence of solid catalysts is due to a major change in the reaction mechanism, as usually happens in heterogeneous catalysis, it follows that in the presence of the catalyst the rate of reaction does not change much relative to the rate in the empty reactor and that the selectivity of the process does not change appreciably (Table 7). For the latter reason, it is also difficult to suppose that the role of the catalyst consists in chain termination for the competing reaction. The more likely hypothesis is that the reaction mechanism remains largely unchanged; the reaction takes place in the bulk-phase but the active surface accelerates the slowest stages.

Table 7. Effects of solid catalysts on oxidative dehydrogenation (hydrocarbon : oxygen : nitrogen = 1 : 1 : 10, temperature 530–540°C).

Catalyst	Specific surface, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Yields, % of divinyl from n-butane $\varphi = 0.03$* w.r.t. starting material	Yields, % of divinyl from n-butane $\varphi = 0.03$* w.r.t. product	Yields, % of isoprene from isopentane $\varphi = 0.08$ w.r.t. starting material	Yields, % of isoprene from isopentane $\varphi = 0.08$ w.r.t. product	Yields, % of benzene from n-hexane $\varphi = 0.04$ w.r.t. starting material	Yields, % of benzene from n-hexane $\varphi = 0.04$ w.r.t. product
Empty reactor **	—	—	9	47	6	37	6	17
Quartz	0.01	—	8	66	13	60	7	20
Silica gel I	24	0.79	24	76	3	12	18	49
Silica gel II	120	0.83	23	67	—	—	—	—
Alumina	190	0.77	<1	<1	<1	<1	10	30
Alumina	56	0.67	3	8	—	—	—	—
5% KBr and 1% AgI on silica gel I	25	0.7	13	47	—	—	—	—
5% KBr and 1% AgI on quartz	20	0.72	33	73	5	20	16	51
	0.1	—	9	51	18	58	—	—

* φ is the iodine : hydrocarbon molar ratio.

** At the same flow rate as in the experiments with catalysts.

Kolobikhin et al.[172] believe that the accelerating effect of solid catalysts on the oxidative dehydrogenation of n-butane in the presence of oxygen and added iodine is associated with the catalysis of the oxidation [according to the overall Eqn. (4)] of the hydrogen iodide formed in the dehydrogenation. Indeed, solid materials such as broken quartz, silica gel, and other silicon-containing substances catalyse the oxidation of hydrogen iodide with oxygen[174–177]. However, this finding alone is insufficient to explain the activating effect of catalysts; one might expect the acceleration of the oxidative dehydrogenation by catalysts for the oxidation of hydrogen iodide only if the hydrogen iodide oxidation stage was the slowest in oxidative dehydrogenation, but this is not confirmed experimentally (see subsection 3b). Indeed the present author's data[164] show that there is no parallel variation of the activity of the catalyst in oxidative dehydrogenation and the acceleration of the oxidation of hydrogen iodide.

It follows from Tables 6 and 7 that the wide differences in the effect of the porous structure on the reactions of n-butane, isopentane, and n-hexane are associated mainly with the secondary reactions of unsaturated products[161]. The present author investigated[161] the reactions of divinyl and isoprene on quartz, silica gels, and alumina. Divinyl and isoprene are converted mainly into coke-like and tarry products. At 530°C, with the ratios divinyl : iodine : oxygen : nitrogen = 1 : 0.03 : 1 : 10 and a duration of contact of 0.6 s, 22% and 42% of divinyl react respectively in the empty reactor and in the presence of silica gel. Therefore the increased yield of divinyl in the dehydrogenation of n-butane in the presence of silica gel, relative to the empty reactor (Table 7), cannot be due to the inhibition of the decomposition of the divinyl formed. Under these conditions almost complete reaction of divinyl was observed on γ-alumina, which probably accounts for the absence of divinyl from the n-butane reaction products on this catalyst.

Isoprene enters into secondary reactions much more readily than divinyl and this probably explains the decrease of its yield with increasing porosity of the catalysts, this being observed both in experiments with small amounts of iodine (Table 7) and in the presence of acceptors (Table 6). Thus the effect of the solid catalyst on oxidative dehydrogenation in the presence of iodine and oxygen is complex and probably consists in the acceleration of the slow stage of the process and in the participation of the catalyst in secondary reactions of the products.

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In recent years significant advances have been achieved in the field of oxidative dehydrogenation of hydrocarbons. Conditions have been found under which the formation of dehydrogenation products in considerable yields is the dominant process in the reaction between the hydrocarbon and an oxidising agent. The oxidising agents may be oxygen or halogens and also substances which give rise to them on decomposition.

On interaction with oxygen, the dehydrogenation of mono-olefins to more unsaturated hydrocarbons takes place in the presence of heterogeneous catalysts. There are virtually no such catalysts for the dehydrogenation of saturated hydrocarbons. The use of iodine-containing substances even in small amounts makes it possible to dehydrogenate fairly readily not only olefins but also saturated hydrocarbons. An increase in the degree of unsaturation of the product is favoured by the introduction into the reaction zone of hydrogen iodide acceptors.

Solid catalysts which are not acceptors and which are capable of accelerating appreciably the oxidative dehydrogenation of saturated hydrocarbons are also known, but their effect on the process is radically different from that of the catalysts for the oxidative dehydrogenation of olefins. While the latter is a typical heterogeneous-catalytic reaction, the homogeneous chain-radical mechanism probably persists in the presence of catalysts suitable for oxidative dehydrogenation of saturated hydrocarbons and the role of the solid surface may consist in the acceleration of the slowest stages of the process.

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Condensation of Unsaturated Compounds with Formaldehyde (the Prins Reaction)

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CONTENTS

1. Synthesis of 1,3-dioxans from olefins in the presence of acid catalysts 17
2. Synthesis of 1,3-dioxans from aryl-substituted olefins 18
3. Synthesis of 1,3-dioxans from halogeno-olefins 19
4. Synthesis of 1,3-dioxans from cyclic olefins 19
5. Synthesis of 1,3-dioxans from diolefins 20
6. Synthesis of 1,3-dioxans from enyne and dienyne hydrocarbons 22
7. The mechanism of the Prins reaction 22
8. Properties and applications of 1,3-dioxans 22
9. Infrared spectra of substituted 1,3-dioxans 23
10. Synthesis of 1,3-dioxans from terpene hydrocarbons 23

In their review Arundale and Mikeska[1] made a thorough compilation of extensive data on the reaction of olefins with aldehydes and the use of the reaction products in organic synthesis. In recent years numerous papers have appeared in the scientific literature dealing with the mechanism and the chemistry of the Prins reaction and also the possibility of using ion-exchange resins as catalysts, first demonstrated in our laboratory[2].

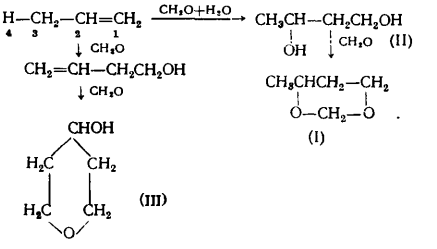
We attempted to review the literature for the period 1953–1965.

1. SYNTHESIS OF 1,3-DIOXANS FROM OLEFINS IN THE PRESENCE OF ACID CATALYSTS

a. Condensation of Olefins with Formaldehyde† in the Presence of Acid Catalysts

In the presence of acid catalysts the main products are 1,3-dioxan and 1,3-glycol. The highest rate of condensation is observed in the reaction of isobutene with formaldehyde. Tertiary olefins with high molecular weights, straight-chain olefins, and also higher aldehydes are less reactive. Apart from the acid catalysts used earlier for the reaction (sulphuric, acetic, hydrochloric, and hypochlorous acids), nitric acid[3] and KU-2 cation-exchange resin[2] have been employed.

In the reaction between propene and formaldehyde investigated by Farberov and coworkers[4,5] optimum conditions are attained at sulphuric acid concentrations of 1–5 wt. %. In the presence of acid of this concentration the main products are 4-methyl-1,3-dioxan (I) (85% yield), butane-1,3-diol (II) (3–5% yield), 1-hydroxytetrahydropyran (III) (7–8% yield), and traces of allylmethanol:



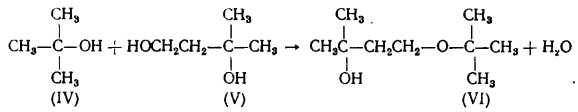
According to the hypotheses put forward by Nesmeyanov and Kabachnik[6], olefins of this type are characterised by

† In some cases formaldehyde is denoted by fa.

the presence of σ, π-conjugation, as a result of which they are capable of two types of reaction, at 1,2- and 1,4-bonds. On the other hand, with isobutene virtually only 1,2-addition takes place (evidently because of the higher rate of this reaction). 4-Acetoxytetrahydropyran was obtained in the condensation of propene in the presence of acetic acid[7]. Isobutene readily condenses with various aldehydes, a complex mixture of products, from which 26 different compounds were isolated, being formed in addition to the main reaction products 1,3-dioxan and 1,3-glycol[8,9].

There exist two views concerning the mechanism of the formation of the dioxan and diol under the conditions of the Prins reaction. In later studies it was assumed that the dioxan and diol may form simultaneously[10]. The mechanism of the Prins reaction will be discussed in detail below.

In the condensation of isobutene with formaldehyde a considerable amount of t-butyl alcohol (IV) forms, and under the conditions of the Prins reaction the latter can react with the 3-methylbutane-1,3-diol (V) produced to give 2-hydroxy-2-methyl-4-t-butoxybutane (VI):



Trenke and Nemtsov[11] were the first to draw attention to this reaction. They hydrolysed the hydroxy-ether obtained in an acid medium both in the presence and in the absence of formaldehyde. t-Butyl alcohol and 3-methylbutane-1,3-diol were obtained in the first case. Hydrolysis in the presence of formaldehyde gave 4,4-dimethyldioxan and t-butyl alcohol; at 98°C the hydrolysis is extensive and rapid in both cases.

Methyldihydropyran and the isomeric methylenetetrahydropyran were also found in the products of the condensation of isobutene and formaldehyde[11,12]. Under the reaction conditions methyldihydropyran reacts with formaldehyde to form a compound containing the pyran and dioxan rings–methyltrioxaperhydronaphthalene[12-14]. In the same papers it is stated that the reaction products contain 4-methyl-4-vinyl-1,3-dioxan and methyldioxanyldioxan.

Under the conditions of the Prins reaction there is also the possibility of the occurrence of the Cannizaro–Tishchenko side-reaction, in which formic acid is formed from formaldehyde and water:

$$2\,CH_2O + H_2O \rightarrow HCOOH + CH_3OH\,.$$

The loss of formaldehyde by this reaction was investigated by Farberov and Speranskaya[15].

The concentration of sulphuric acid used as the catalyst and the reaction temperature have a profound effect on the yield of the main products. The study of the effect of the concentration of the acid on the rate of reaction showed that the latter is proportional to the acid concentration[10]. However, in order to improve the selectivity of the process, it is preferable to use dilute acid solutions (up to 5 wt.%)[4,5]. The Prins reaction also takes place at room temperature, but useful rates of conversion of isobutene are attained only at 70–100°C.[16]

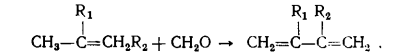
It has been stated in recent communications that, apart from sulphuric acid, cation-exchange resins can be used as catalysts in this reaction[2,17-20]. The application of Amberlite IR-120 and KU-2 resin (the latter produced in the USSR)[21] resulted in a 56% yield of dimethyldioxan with respect to the unreacted olefin. Ion-exchange resins as catalysts have a number of advantages, which are particularly important in the industrial application of the process.

Compared with isobutene, straight-chain butenes are much less reactive. In the condensation of a mixture of butenes, containing 20% of isobutene and 37% of straight-chain butenes, with formaldehyde during 5 h at 70°C, 70% of isobutene and only 3% of butenes reacted[17], but-2-ene reacting somewhat faster than but-1-ene[9,22]. In 3 h at 90°C 4-ethyl-1,3-dioxan was obtained from but-1-ene in 34% yield and a mixture of *cis*- and *trans*-isomers of 4,5-dimethyl-1,3-dioxan was obtained from but-2-ene in 74% yield. According to Farberov's data[4], straight-chain butenes are approximately equally reactive.

The condensation of pentenes with formaldehyde was investigated very recently using KU-2 cation exchanger as catalyst[23]. Substituted 1,3-dioxans are formed. The dioxan fraction (b.p. 152–154°C, yield 66.3%) isolated from the reaction products consisted of 4,4,5-trimethyl-1,3-dioxan and 5-ethyl-4-methyl-1,3-dioxan. t-Pentyl alcohol was also isolated from the products. The reactivities of the isomeric pentenes have been compared.

b. Condensation in the Presence of Heterogeneous Acid Catalysts at High Temperatures

This method has been described only in the patent literature[24-31]. It consists essentially in passing the olefin, aldehyde, and an inert diluent at 250–400°C over heterogeneous catalysts. Under these conditions, diene hydrocarbons are produced:



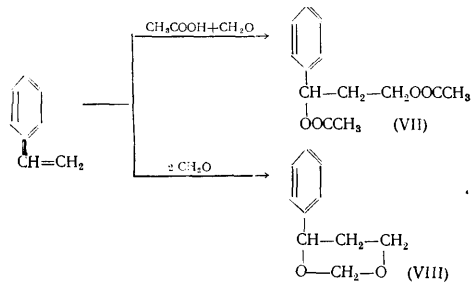
The best results were obtained when olefins with a tertiary carbon atom were used.

The reaction is carried out in the presence of a large excess of olefin (olefin : formaldehyde = 8 : 1), probably in order to suppress side-reactions, which lead to the formation of high-molecular-weight oxygen-containing products. In addition, the reaction products are diluted with a large volume of an inert diluent (nitrogen, carbon dioxide, lower saturated hydrocarbons) to suppress the polymerisation and condensation reactions. In this method the catalysts are mineral acids deposited on activated alumina, silica gel, magnesium oxide, or boron trioxide, synthetic catalysts for the cracking of petroleum, etc. The reactions take place at the normal or elevated (up to 7 atm) pressures. 4,4-Dimethyldioxan is also obtained in the condensation of isobutene with formaldehyde, using silica gel or aluminosilicates as catalysts at 500°C.[32] The acidity of the catalyst has a decisive effect on the yield of the main product in this case. Thus at $H_0 = 1.5$–3.8 (silica gel) a 97% yield of 4,4-dimethyldioxan was obtained.

2. SYNTHESIS OF 1,3-DIOXANS FROM ARYL-SUBSTITUTED OLEFINS

The literature dealing with the condensation of aryl-substituted and cyclic olefins was not reviewed by Arundale and Mikeska[1]. The condensation of styrene with formaldehyde in the presence of a mixture of sulphuric and glacial acetic acids was first investigated by Prins[33]. As a result of the condensation, he obtained the diacetate of

1-phenylpropane-1,3-diol and a certain amount of 4-phenyl-1,3-dioxan:

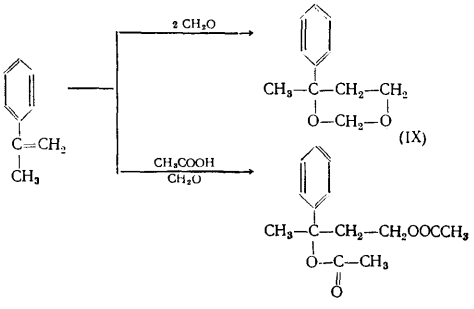


However, Prins erroneously regarded these compounds as derivatives of 2-phenylpropane-1,3-diol. Their true structure was established later[34].

It is noteworthy that, when the reaction is carried out in acetic acid solution, the yield of 4-phenyl-1,3-dioxan (VIII) is reduced due to the formation of the acetates of 1-phenylpropane-1,3-diol (VII). When 1,4-dioxan is used as the solvent, the yield of 4-phenyl-1,3-dioxan is increased to 78%.[35] With hydrochloric acid as the catalyst[36], the reaction can be carried out also in an inert hydrocarbon solvent. 4-Phenyldioxan was obtained in 88% yield by the condensation of styrene with a 37% solution of formaldehyde in the presence of sulphuric acid[35].

Backer[37] noted that the reaction of α-methylstyrene with formaldehyde in a mixture of 100% sulphuric and glacial acetic acids at 40°C is accompanied by extensive polymerisation of α-methylstyrene. Polymerisation can be partially suppressed if the reaction is performed at 0°C, but at this temperature the conversion of α-methylstyrene is low.

The reaction of α-methylstyrene with formaldehyde in the presence of a mixture of sulphuric and acetic acids has the following mechanism:



If orthophosphoric acid is used as the catalyst, the yield of 4-methyl-4-phenyl-1,3-dioxan (IX) can be increased to 75% with respect to the aldehyde.

4-Acetoxy-2-phenylbut-1-ene was obtained in 70% yield in the condensation of α-methylstyrene with formaldehyde in the presence of acetic acid[38]. Farberov[4] showed that the condensation of α-methylstyrene with formaldehyde is quite possible in the presence of 1–1.5% sulphuric acid. Here the yield of 4-methyl-4-phenyl-1,3-dioxan was 85%. In their study of the products of the reaction of anethole with formaldehyde by the NMR method, Smissman et al.[39] noted only the formation of the *cis*-isomers of 1,3-dioxan.

A detailed study of the condensation of α-methylstyrene with formaldehyde was made by French chemists[40], who used various methods for the identification of the chemical compounds (infrared spectroscopy, preparative chromatography, etc.) and isolated and described 15 compounds formed in this system. The reaction of α-methylstyrene with 37% aqueous solution of formaldehyde in the presence of KU-2 resin as the catalyst has been investigated[41].

3. SYNTHESIS OF 1,3-DIOXANS FROM HALOGENO-OLEFINS

Monohalogeno-olefins can react with formaldehyde to form halogeno-1,3-dioxans. 4-Chloromethyl-4-methyl-1,3-dioxan and 3-chloromethylbutane-1,3-diol are formed in the condensation of methylallyl chloride with paraformaldehyde in the presence of sulphuric acid or $BF_3.O(C_2H_5)_2$.[42]

Farberov and coworkers[43] investigated in detail the reaction of chloropropenes with paraformaldehyde under various conditions. The first attempts to prepare halogeno-substituted aryl-1,3-dioxans from halogenostyrenes proved unsuccessful. Beets and Drukker[44] failed in their attempt to condense α- and β-bromostyrenes with formaldehyde in the presence of 5% sulphuric acid. When 50% sulphuric acid was used, 4-aryl-5-halogeno-1,3-dioxans were obtained in 60–90% yield[45].

The work of Japanese and Italian chemists dealing with the condensation of β-bromostyrene and β-bromo-*p*-nitrostyrene with paraformaldehyde was published comparatively recently[46-48]. These studies are of great theoretical interest, since they led to the correction of certain aspects of the mechanism and stereochemistry of the Prins reaction. It is known that the electrophilic addition to carbon–carbon double bonds takes place in the *trans*-position, and this also holds for the Prins reaction.

It was shown in the above investigations that under certain conditions the Prins reaction is stereospecific, i.e. involves *cis*-addition. Thus *cis*-5-bromo-4-phenyl-1,3-dioxan was obtained in the condensation of *trans*-β-bromostyrene with paraformaldehyde.

While the condensation of monohalogeno-olefins with formaldehyde in the presence of dilute mineral acids leads to the formation of halogenated 1,3-dioxans, polyhalogeno-olefins give halogeno-substituted hydroxy-acids or alcohols, depending on the nature and concentration of the catalyst. Halogeno-substituted hydroxy-acids and their esters are obtained in the condensation of di-, tri-, and tetra-chloroethylene with formaldehyde in the presence of dilute sulphuric acid[49]. The condensation of the same olefins with paraformaldehyde in the presence of hydrochloric acid yields chloropropanols[50]. When paraformaldehyde is condensed with trichloroethylene in the presence of aluminium chloride as the catalyst, $\alpha\beta$-dichloropropionic acid, 2,3,3,3-tetrachloropropan-1-ol together, and di(2,3,3,3-tetrachloropropyl) ether are obtained[51].

4. SYNTHESIS OF 1,3-DIOXANS FROM CYCLIC OLEFINS

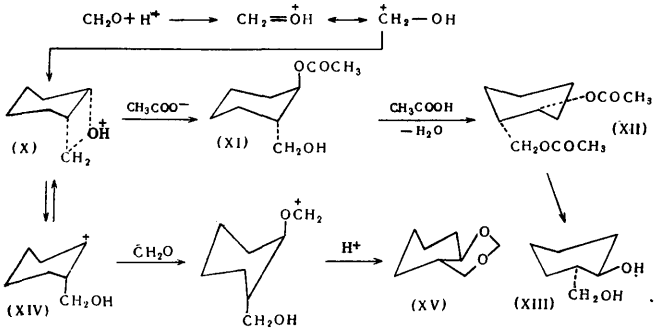
Arundale and Mikeska[52] were the first to show that in the presence of 45–55% sulphuric acid it is possible to condense cyclic olefins with formaldehyde to form 1,3-dioxans. When the reaction is carried out in the presence of sulphuric and acetic acids, the products include, together with 1,3-dioxans, a complex mixture, the main components of which are the diacetate of 2-hydroxymethylcyclohexanol, 3,4-tetramethylene-2,5-dihydrofuran, and 1-hydroxymethylcyclohexene[53-59].

Blomquist and Wolinsky[58] and Smissman and Mode[60] showed that the condensation of cyclohexene with formaldehyde in the presence of acid catalysts is a special case

of the electrophilic addition of an aldehyde to an olefin double bond[61-63]. The above workers noted that only the *trans*-isomers are formed in the reaction of cyclohexene with formaldehyde.

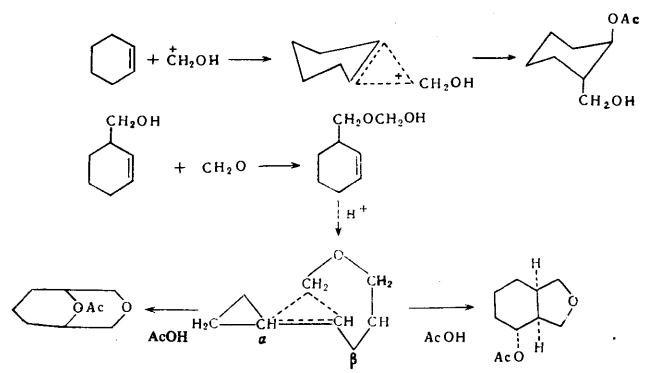
The high stereospecificity of the Prins reaction leads to the formation exclusively of *trans*-2-hydroxymethylcyclohexanol and also substituted 3-oxabicyclononanes in which the substituent in the hydrocarbon ring is in the *trans*-position relative to the heterocycle formed by *cis*-closure.

Blomquist and Wolinsky proposed a mechanism for the Prins reaction, which accounts for its stereoselectivity[58]. As a result of the protonation of formaldehyde and the attack by a solvated carbonium ion on the olefin double bond, a hybrid oxonium–carbonium ion, (X) ⇌ (XIV), is formed. The acetate ion attacks the oxonium–carbonium ion (X) from the least screened side, which leads to the formation, via a diaxial monoacetate stage (XI), of *trans*-diequatorial diacetate (XII), whose hydrolysis yields the diol (XI); the attack of formaldehyde on the carbonium ion (XIV) and subsequent cyclisation yield *trans*-1,3-dioxan (XV):



However, this mechanism does not explain the formation of side-products.

Dolby[59] proposed another mechanism for the Prins reaction. The intermediate product, which in Dolby's view controls the stereochemistry of the reaction, is a three-membered cyclic ion, analogous to the intermediate products suggested by other workers for electrophilic addition at the double bond:



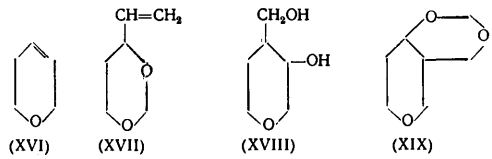
Smissman and coworkers studied the mechanism and the stereospecificity of the Prins reaction using the condensation of anethole with formaldehyde in the presence of an acid catalyst as an example[64,65].

The Prins reaction has been extended to the condensation of olefins not only with aldehydes but also with ketones. Fodor and coworkers[66] showed that 2-(α-hydroxyisopropyl)cyclohexanol forms (after hydrolysis) in the reaction of cyclohexene with acetone in the presence of sulphuric acid.

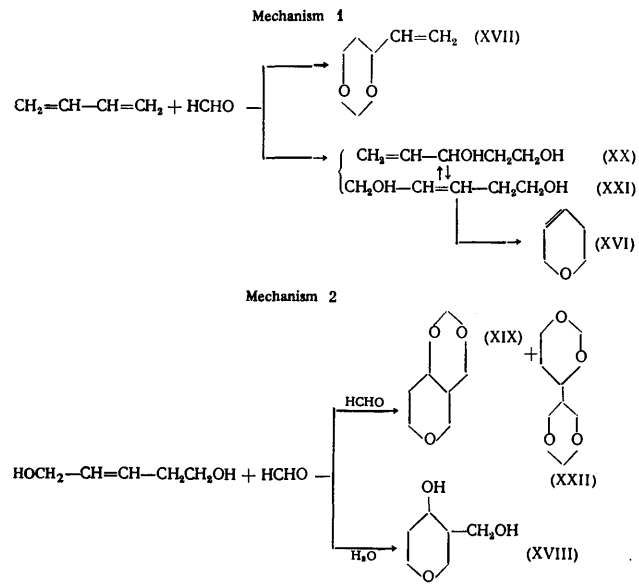
The condensation of cyclohexene and other cyclic olefins with formaldehyde in the presence of KU-2 cation-exchange resin has been investigated[67].

5. SYNTHESIS OF 1,3-DIOXANS FROM DIOLEFINS

A very small number of papers dealing with the condensation of diolefins with formaldehyde has been published. In 1955 Hanschke[68] showed that the condensation of butadiene with two moles of formaldehyde in the presence of sulphuric acid at 80°C yields a mixture of products, from which he isolated and identified 5,6-dihydro-2*H*-pyran (XVI), 4-vinyl-1,3-dioxan (XVII), tetrahydro-4*H*, 5*H*-pyrano[3,4-*d*]-1,3-dioxan (XIX), and the corresponding glycol (XVIII).



Extensive studies on the Prins reaction have been made in recent years at the French Petrochemical Institute. At the end of 1964 Hellin et al.[69] at this Institute published a paper describing the butadiene–formaldehyde system under the conditions of the Prins reaction. They studied the reaction at 80°C in aqueous sulphuric acid with the molar ratio formaldehyde : butadiene = 2; the duration of the reaction was varied from 30 min to 4 h. The authors quote the following two reaction mechanisms:

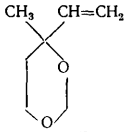


In mechanism 1 two isomers of pentenediol (XX) and (XXI) are formed as a result of 1,2- or 1,4-addition to butadiene. Of these isomers, the second, which has two primary hydroxyls and a double bond within the chain, [isomer (XXI)] is the more likely. Dihydro-5,6-α-pyran (XVI), which is one of the main products of the Prins reaction, forms on intramolecular conversion of pent-2-ene-1,5-diol (XXI) into an ether.

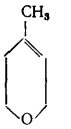
The multiplicity of the possible modes of the reaction leads to the formation of higher condensation products. In particular, diols with a double bond (see mechanism 2)

can react directly with formaldehyde to form large molecules—*trans*-trioxaperhydronaphthalene (XIX), dioxanyldioxan (XXII), and *trans*-hydroxyethyltetrahydropyranol (XVIII). The simultaneous presence of trioxaperhydronaphthalene and dioxanyldioxan confirms the above view rather than the possible occurrence in this case of the Prins reaction with 4-vinyl-1,3-dioxan.

The reaction with isoprene is even more complex[70]. The primary products are 4-methyl-4-vinyl-1,3-dioxan (XXIV) and 4-methyldihydro-5,6-pyran (XXV),

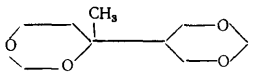


(XXIV)

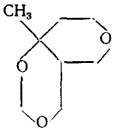


(XXV)

whose subsequent reactions lead to the appearance of more complex products: 5-(4′-methyl-1′,3′-dioxan-4′-yl)-1,3-dioxan (XXVI), *cis*- and *trans*-10-methyl-1,3,7-trioxaperhydronaphthalenes, and the corresponding diols:



(XXVI)



(XXVII)

In the USSR the reaction of diene hydrocarbons with formaldehyde in the presence of hydrochloric acid was investigated by Ustavshchikov and Fel'dblyum[71]. The reaction was studied mainly using butadiene (divinyl). The main reaction products were isolated and characterised. The reaction of the closest butadiene homologues, piperylene and isoprene, were studied in less detail. The reaction was carried out for 3–5 h at 20°C with the molar ratios diene : CH_2O : HCl = 1 : 1 : 2. It was established, on the basis of the rate of disappearance of formaldehyde, that piperylene and isoprene react approximately 1.5 times faster than divinyl.

In the reaction with divinyl the main products are 4-vinyl-1,3-dioxan, 3-chloromethyl-4-chlorotetrahydropyran, and the formals of the isomeric unsaturated chlorohydrins, for example 1-chloropent-2-en-5-ol. The cyclic formal of 3-hydroxymethyltetrahydropyran-4-ol was also isolated in small amounts.

In contrast to divinyl, piperylene and isoprene are mainly hydrochlorinated under the reaction conditions with formation of isomeric chloropentenes; 1,3-dioxans and the corresponding dichloro-derivatives of alkyl-tetrahydropyrans are also formed.

On the basis of their results, the authors proposed the following mechanism for the reaction between dienes and formaldehyde. Apparently the initial step is the protonation of the oxygen atom of formaldehyde:

$$\overset{+}{H} + O{=}CH_2 \rightleftarrows HO\overset{+}{C}H_2 .$$

The hydroxymethylcarbonium ions attack the diene molecules with formation of the carbonium ions A and B,

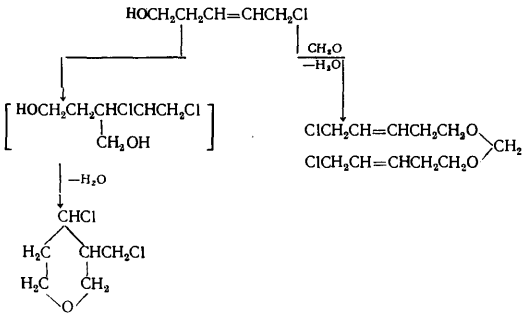
$$CH_2{=}CH{-}CH{=}CH_2 + \overset{+}{C}H_2OH \longrightarrow \begin{cases} \overset{+}{C}H_2{-}CH{=}CH{-}CH_2CH_2OH & (A) \\ CH_2{=}CH{-}\overset{+}{C}H{-}CH_2CH_2OH . & (B) \end{cases}$$

whose reaction with formaldehyde or a chloride ion leads to the formation of 1,3-dioxan or chlorohydrin respectively:

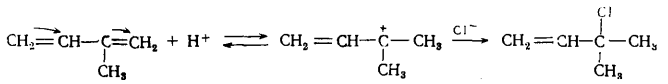
$$\overset{+}{C}H_2{-}CH{=}CH{-}CH_2CH_2OH \xrightarrow{Cl^-} ClCH_2{-}CH{=}CH{-}CH_2CH_2OH$$

$$CH_2{=}CH{-}\overset{+}{C}HCH_2CH_2OH \xrightarrow[-H^+]{CH_2O} CH_2{=}CH{-}\underset{\displaystyle O{-}CH_2{-}O}{\overset{\displaystyle |}{CH}}{-}CH_2{-}CH_2$$

Dioxan has actually been isolated as one of the reaction products. The chlorohydrin probably undergoes secondary reactions by the mechanism



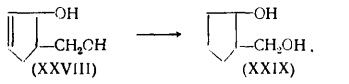
When the diene is isoprene or piperylene, the protons can also react directly with the latter, which leads to the formation of carbonium ions derived from hydrocarbons and the final products are chloropentenes:



However, the mechanism of the formation of the other products is the same.

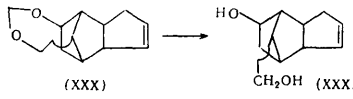
Beets and Drukker[44] investigated the reaction of cyclopentadiene with formaldehyde. When the reaction was carried out in an autoclave at 185°C without catalysts, only a resinous product was obtained. When cyclopentadiene was treated with an excess of 36% aqueous solution of formaldehyde in the presence of sulphuric acid, the authors obtained 2-hydroxymethylcyclopent-4-enol (XXVIII) in 20% yield and the corresponding dioxan. The cyclopentadiene reacted completely; also present were high-boiling products, from which the pure components could not be isolated. When the amount of formaldehyde per mole of diene was reduced from 2.72 to 1.23 moles, the yield of the corresponding dioxan fell and the amount of hydroxylated high-boiling products increased.

2-Hydroxymethylcyclopent-4-enol (XXVIII) was also obtained on heating cyclopentadiene in acetic acid solution with formaldehyde in the presence of catalytic amounts of toluenesulphonic acid. Its structure was demonstrated by conversion into the saturated diol (XXIX) by catalytic hydrogenation:



(XXVIII) (XXIX)

Zimmermann and Reiners described the Prins reaction with dicyclopentadiene[73]. They carried out the reaction in formaldehyde solution in the presence of sulphuric acid at 80°C. The dioxan (XXX) probably forms under the reaction conditions. The diol (XXXI) was obtained by the reaction of the same compound with an excess of methyl alcohol and a small amount of sulphuric acid:



(XXX) (XXXI).

6. SYNTHESIS OF 1,3-DIOXANS FROM ENYNE AND DIENYNE HYDROCARBONS

The first studies on the condensation of enyne and dienyne hydrocarbons with formaldehyde in the presence of sulphuric acid were made by Matsoyan and Saakyan[74]. It was established that formaldehyde reacts selectively with dienes, the reaction involving exclusively the substituted double bond of the divinylacetylene hydrocarbon. During the condensation substituted 1,3-glycols are formed in small amounts as side-products, but they are difficult to purify.

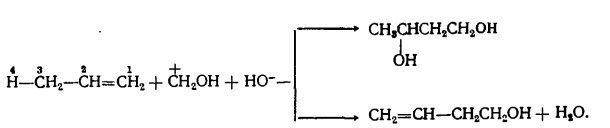
The reaction of formaldehyde with tertiary vinylacetylene alcohols was carried out using KU-1 and KU-2 cation-exchange resins as the catalysts[75]. It was shown that in this case the main products are 1,3-dioxans and a small amount of 1,3-glycols of the vinylacetylene series. The authors of the present review made a detailed study of the optimum conditions for the condensation of ethynyldimethylvinylmethanol with formaldehyde in the presence of KU-2 cation-exchange resin[76].

7. THE MECHANISM OF THE PRINS REACTION

Franzen and Krauch[77] believe that the initial step in the reaction is the addition of a proton to the oxygen atom of the carbonyl group with formation of the carbonium ion $R-\overset{+}{C}-OH$, which then attacks the double bond at the site of the highest electron density. The new carbonium ion can react further in three ways. In the interaction with an excess of the aldehyde, dioxan is produced, the reaction with water leads to the formation of a glycol, and, finally, the removal of a proton results in the formation of an unsaturated alcohol. The glycol and dioxan are formed independently of one another; although the glycol can, in fact, be produced from 1,3-dioxan, under the reaction conditions this happens rarely.

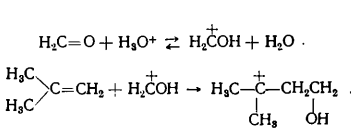
The third reaction, i.e. the removal of a proton, is observed only in the addition of formaldehyde. A proton is removed (in accordance with the Hofmann rule) from the carbon atom adjacent to the carbonium centre which has the smallest number of substituents. The removal of a proton from the CH_3 group can be facilitated by the presence of a hydroxyl. The formation of the glycol greatly depends on the basicity of the medium, since at high pH values the 1,3-glycol decomposes into an olefin and an aldehyde.

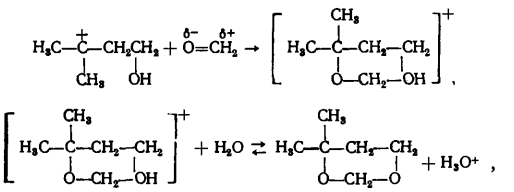
According to Farberov's hypotheses[4,5], the diol results from the reaction at 1,2-bonds and the unsaturated alcohol from the reaction at 1,4-bonds:



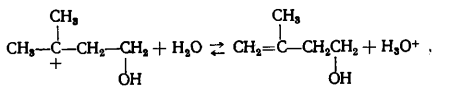
Generalising the results obtained, the following general mechanism of the Prins reaction can be put forward[20,78], for isobutene and formaldehyde as examples:

a. main reaction:

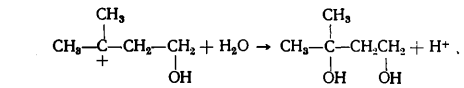




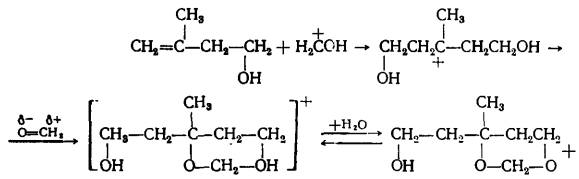
b. side-reactions:



(1)

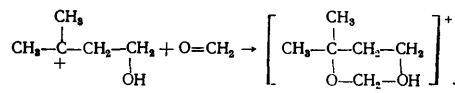


(2)



(3)

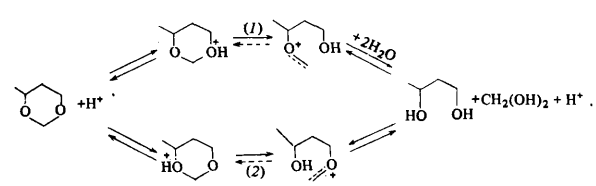
Kinetic studies show that the reaction on ion-exchange resins is of third order, and the rate-limiting stage is the reaction of the secondary carbonium ion with the aldehyde[20]



8. PROPERTIES AND APPLICATIONS OF 1,3-DIOXANS

1,3-Dioxans are widely used as the starting materials for the synthesis of varnishes[79], resins[80], detergents[81], antibiotics[46,47], and insecticides[82]. In practice the most important are the syntheses of diene hydrocarbons based on them. Since hydrolysis is an intermediate stage of the conversion of alkyldioxans into dienes, a number of papers dealing with this problem has appeared in recent years in the scientific literature. In the hydrolysis (methanolysis) of alkyl-1,3-dioxans in the presence of small amounts of sulphuric acid and an excess of methyl alcohol, it proved possible to isolate diols in yields of up to 80%.[83] However, the hydrolysis of alkyldioxans in which the oxygen atom is linked to a tertiary carbon atom is much more difficult. The yield of the diol is at best not more than 50%. Using a cation exchanger instead of sulphuric acid in the methanolysis of 4-methyl-1,3-dioxan, the diol was obtained in quantitative yield[84].

The kinetics of the hydrolysis of a number of substituted 1,3-dioxans in water and aqueous dioxan have been investigated at 60–70°C.[85-87] The hydrolysis of 1,3-dioxans can take place in two ways:



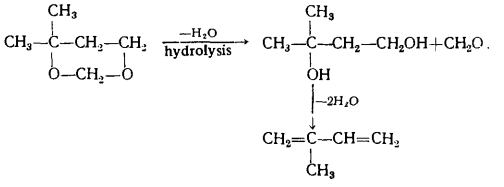
Kinetic measurements show that the first mode of reaction is the more likely.

Dehydration of glycols leads to the formation of the corresponding diene hydrocarbons, but since the yield of glycols is low because of hydrolysis, this method is unsuitable for the industrial manufacture of diene hydrocarbons. Therefore another procedure was chosen, which permits the synthesis of diene directly in one stage—the catalytic dissociation of alkyldioxans in the presence of suitable catalysts. The choice of the catalyst capable of selective dissociation of the alkyldioxan with a high activity was difficult because reactions of this kind had not been investigated in chemical engineering.

The patent literature describes methods of synthesising dienes on the basis of dioxans[1], but in the scientific literature this process had not been elucidated until the publication of the work of Farberov and coworkers[88]. In the course of their studies over a number of years on the synthesis of isoprene from isobutene and formaldehyde, they investigated in detail the catalytic dissociation of 4,4-dimethyl-1,3-dioxan to isoprene in the gas phase over a solid catalyst.

Best results were obtained when Group II metal phosphates were used as catalysts, in particular calcium phosphates. These catalysts are very active and selective, exhibit high productivity, and are fairly stable. An essential condition is that the process be carried out in the presence of water vapour, which is probably connected with the dehydration of acid calcium phosphates.

Bearing in mind that an increase in the concentration of water vapour in the reaction mixture results in an acceleration of the catalytic dissociation of dimethyldioxan, Farberov proposed a mechanism, according to which water participates directly in the reaction. As a result of the reaction with water, dimethyldioxan is hydrolysed on the catalytic surface to the diol, which is then dehydrated to give isoprene:



As a result of a detailed study of the conditions of the catalytic dissociation of dimethyldioxan [at 375°C, 1 : 14 (molar ratio) dilution with water vapour, volume flow rate of dimethyldioxan 0.7 ml per ml of catalyst per hour] isoprene yields of 75–85% with respect to the dioxan passed through and 80–85% with respect to the dioxan decomposed were attained. The method thus developed served as the basis of the industrial manufacture of isoprene of a high degree of purity.

9. INFRARED SPECTRA OF SUBSTITUTED 1,3-DIOXANS

The available data on the infrared spectra of 1,3-dioxans reveal a very complex structure of the bands, the number of characteristic bands being variable[21,89,90]. 1,3-Dioxans substituted in position 4 constitute a system characterised by four bands[85]: two very intense bands in the region 1166 ± 20 cm^{-1} and 1037 ± 15 cm^{-1} and two other less intense bands in the region 1090 ± 25 cm^{-1} and 985 ± 10 cm^{-1}.

10. SYNTHESIS OF 1,3-DIOXANS FROM TERPENE HYDROCARBONS

Until recently the behaviour of the extensive class of terpene hydrocarbons in the Prins reaction was virtually uninvestigated, although the possibility of the condensation of aldehydes with olefins was first demonstrated by Prins for α-pinene and camphene as examples[91]. However, Prins did not investigate these reactions in detail and merely indicated the physicochemical characteristics of some of the condensation products (without stating the yield). Serious studies on the condensation of α-pinene, camphene, dipentene, and β-pinene were begun by Japanese chemists. Watanabe, who studied the condensation of formaldehyde with α-pinene in a mixture of acetic and phosphoric acids and acetic anhydride, obtained a mixture of the acetates of α-terpineol, (±)-isoborneol, and 6-acetoxymethyl-$\Delta^{1,8(9)}$-*p*-pentadiene, whose structure was demonstrated by its further conversion into (±)-carbomenthone[92].

On the other hand, when a mixture of α-pinene, formaldehyde, and 60% perchloric acid was stirred for 6 h at 95–100°C, 1-methyl-4-(4′-methyl-1′, 3′-dioxacyclohex-4′-yl)cyclohexene (I) and bisdioxan $C_{14}H_{24}O_4$ (II) were obtained. The structure of the products (I) and (II) was confirmed by hydrogenation[92].

Using various catalysts (98% sulphuric acid, 85% phosphoric acid, 60% perchloric acid), Watanabe and coworkers isolated a mixture of 8-hydroxymethylcamphene and spiro-[2,2-dimethylnorbornane-3,1′-(2′, 4′-dioxacyclohexane)], with an overall yield of 56.3%, in the condensation of camphene with formaldehyde[93].

A complex mixture of products was also obtained in the condensation of dipentene with formaldehyde in the presence of perchloric acid. Apart from the initial products, a fraction boiling at 104–109°C at 7 mmHg was isolated from the reaction mixture freed from impurities by steam distillation. After chromatography on silica, a product was isolated and identified by infrared spectroscopy as a mixture of 1-methyl-4-(4′-methyl-1′, 3′-dioxacyclohex-4′-yl)cyclohexene and 8-isopropyl-1-methyl-2,4-dioxabicyclo[4,4,0]decane, which the authors regard as the primary products of the reaction between dipentene and formaldehyde[94,95]. A complex mixture of products also resulted in the condensation of limonene with paraldehyde in the presence of zinc chloride[96].

The authors of the present review investigated the condensation of α-pinene, dipentene, and camphene with formaldehyde in the presence of KU-2 cation-exchange resin[97].

While the present review was with the editors, a number of communications by the authors of the review dealing with the Prins reaction in the presence of KU-2 cation-exchange resin was published[98–101].

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Electrical and Photoelectric Properties of Organic Polymeric Semiconductors

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CONTENTS

I. Introduction 25
II. Low-molecular-weight organic semiconductors 25
III. Electrical properties of organic semiconducting polymers 26
IV. Photo-semiconducting properties of organic polymers 28
V. Conclusions and prospects 32

I. INTRODUCTION

Organic compounds containing systems of conjugated multiple bonds are now termed organic semiconductors: the conductivity of these substances is electronic, increases exponentially with temperature, and is greater (as a rule) than the conductivity of normal organic compounds.

During the past 10 years, in addition to extensive studies of the semiconducting properties of low-molecular-weight organic compounds, we have witnessed a significant volume of work on the synthesis and characterisation of a new class of organic semiconductors: the macromolecular compounds. The rising interest in semiconducting polymers is due, on the one hand, to recent advances in the physics and technology of inorganic semiconductors, which have led to a search for new materials showing semiconductor properties, and on the other hand to the successful preparation of polymers with a wide variety of physicochemical properties, resulting in widespread applications of polymers in technology. The attractive prospect of developing simple models, leading to a deeper understanding of some biophysical processes (which take place, as a rule, in complex macromolecular systems) has undoubtedly been an additional stimulus to developments in the physics of electronic phenomena in organic systems.

The present review deals with the most important experimental and theoretical data relating to organic semiconducting polymers having an electronic (as distinct from an ionic) conduction mechanism. Since studies on low-molecular semiconductors have led the way to an understanding of the semiconductivity of polymers, we shall briefly review the basic ideas of organic low-molecular semiconductor physics without attempting to cover the literature in detail. The later sections will discuss, separately, the electrical properties of organic semiconducting polymers and photoelectric processes in these materials.

We thought it desirable to devote a whole section to the photoelectronics of organic polymers because the subject is of very recent origin (5 years at the most), and has not so far been reviewed in any way. The aim of this review is to familiarise the reader with the physical aspects of organic polymeric semiconductors.

II. LOW-MOLECULAR-WEIGHT ORGANIC SEMICONDUCTORS

The following basic laws have been shown to apply[1-8] to low-molecular-weight organic semiconductors (dyestuffs, aromatic hydrocarbons):

1. The dark conductivity (σ_d) varies with temperature (T) according to the law

$$\sigma_d = \sigma_0 \exp(-E_d/2kT)\dagger \qquad (1)$$

where σ_0 is a constant for the particular semiconductor, k is Boltzmann's constant, and E_d is the thermal activation energy for dark conduction. E_d usually varies between 0.5 and 3 eV, and the value of σ_d at room temperature can vary between wide limits (10^{-1}–10^{-20} ohm^{-1} cm^{-1}). The thermal activation energy for dark conduction corresponds to the energy of the long-wave edge of the optical absorption curve, and decreases with increasing number of π-electrons in the molecule.

† The form of the exponent depends on the conduction mechanism assumed.

2. Ohm's law is obeyed, in general, up to fields of 10^3 V cm^{-1}, beyond which the current increases faster than linearly with voltage.

3. Polymorphic modifications of a given compound can have substantially different conductivities and activation energies for conduction, and charge carriers of different sign[9,10]. There is evidence of conduction anisotropy (anthracene) in different crystallographic directions.

4. The conductivity increases with increase of pressure up to 100 kg cm^{-2}, but not beyond.

5. Carrier mobilities in organic low-molecular-weight compounds are usually very low (< 1 cm^2 V^{-1} s^{-1}). Hall mobility data for organic semiconductors are extremely rare owing to serious difficulties in the measurement of the Hall effect (the high ohmic resistance of the compounds and possibly also some specific aspect of the conduction mechanism). More recently, a pulse method of measuring mobility in a "sandwich" type of cell has come into use. By this method it has been shown that the mobility in anthracene increases on lowering the temperature, suggesting the possibility of applying the band model (in which this dependence is ascribed to a decrease in the concentration of scattering centres with decrease of temperature).

6. Impurities and defects have a considerable effect on the semiconducting properties of organic semiconductors, but the results of different workers show large discrepancies.

7. The thermoelectric power is independent of temperature, suggesting that the free carrier concentration is independent of temperature.

8. The photoconductivity spectra (particularly in thin layers) and the photo-e.m.f. spectra are usually very similar to the absorption spectra. In thicker layers the photoelectric sensitivity decreases at the absorption maximum. Many experimental results show that a highly developed surface or defects must be present before photoconductivity can appear. These observations suggest that charge carriers are formed either at the surface, when an exciton diffuses towards it, or by the simultaneous interaction of a molecule with two photons or two excitons.

9. The relaxation time of the photoeffect varies over a wide range, from 10^{-6} s to tens of minutes.

10. The photoconductivity (σ_{ph}) increases exponentially with temperature (T) according to the law

$$\sigma_{ph} = \sigma_0 \exp(-E_{ph}/kT) , \qquad (2)$$

where σ_0 is a constant for a particular semiconductor and E_{ph} is the thermal activation energy for photoconduction. The value of E_{ph} usually falls between 0.1 and 0.3 eV, pointing to the presence of bound states from which the carriers must be thermally activated in order to move in the applied electric field. The nature of these states is not fully clear.

11. Current carriers can be injected into organic crystals from various electrodes.

12. The sign of both light and dark carriers in most organic semiconductors so far examined corresponds to positive holes.

13. Vapours and gases can have an appreciable effect on the conductivity and photoelectric sensitivity of the semiconductors.

14. The quantum yield of the photoeffect is not large (10^{-1}–10^{-7} electrons per quantum).

15. Changes in photoconductivity have been observed in a weak magnetic field[11,12].

16. The possibility of forming charge-transfer complexes enables the electronic parameters of the semiconductors to be varied between wide limits.

17. On the basis of the experimental facts listed above, the mechanism of semiconductivity in low-molecular-weight organic compounds is usually associated with overlap of the wave functions of π-electrons from neighbouring molecules. Two basic approaches are usually followed. Some authors have attempted to apply to organic semiconductors the band model which satisfactorily describes electronic phenomena in inorganic semiconductors. Others support the "relay" or "hopping" mechanism of conduction. The distinguishing feature of molecular organic semiconductors is the fact that the interaction forces between separate molecules (van der Waals forces) are much weaker than the interaction forces between the component parts of each molecule, so that the molecules can retain their individuality in the crystal lattice. This gives rise to the exciton type of light absorption, and to the formation of narrow bands of singlet and triplet states in the crystal. These exciton states are satisfactorily described by molecular wave functions rather than by the one-electron Bloch functions used in the band theory. Excitons are neutral entities, and can only be treated as transition states in the formation of free carriers. However, these states are important in conduction when an electron migrating through a crystal can be treated as bound to one of the molecules or missing from it. The nature of these states is determined by the specific features of the lattice of a particular organic semiconductor. An analogous approach can clearly be used to discuss high-molecular weight organic semiconductors, to which the remaining sections are devoted.

III. ELECTRICAL PROPERTIES OF ORGANIC SEMICONDUCTING POLYMERS

The conductivity of organic polymeric semiconductors increases exponentially with temperature according to Eqn. (1). Historically, the earliest publications on organic polymeric semiconductors related to materials obtained by pyrolysis. The electrical conduction of pyrolysed polymers was first observed by Kmetko on heat-treated cellophane[13] and by Winslow and coworkers[14,15] by pyrolysing poly(divinylbenzene) and poly(vinylidene chloride)[14,15].

When organic compounds are heated to 400–650°C, high-molecular-weight compounds are formed from highly unsaturated aromatic molecules[16]. When the temperature is raised still further, large planar networks of atoms packed in fairly random piles are formed, and at very high temperatures (3200°C) these condense into large, highly ordered planes and produce the graphite structure. Thus, graphite can be considered to be the limiting case of a polymeric semiconductor. In spite of fairly detailed studies of these compounds, fully satisfactory mechanisms for the change in their electrical properties with structure and heat treatment have not yet been put forward[17]. Materials prepared at temperatures in excess of 1200°C are usually classified as polymeric carbons. At room temperature, polymeric carbon is an n-type semiconductor with a very narrow forbidden gap (0.07–0.01 eV). The conductivity type changes with temperature, which may be ascribed to the presence in the polymeric lattice of valency-unsaturated non-bridging carbon atoms. Because of this unsaturation, electrons can be extracted from the inner carbon atoms with formation of positive holes as current carriers[18,19].

Materials prepared by heat treatment up to 1200°C are normally classified as pyropolymers. They are usually characterised by a narrow forbidden gap. There have been reports of pyropolymers with conductivities covering the

range from semimetals to dielectrics (10^3–10^{-13} ohm^{-1} cm^{-1}), of n- or p-conductivity type, and mobilities between 10^{-6} and 100 cm^2 V^{-1} s^{-1}.[20]

Pyropolymers prepared from organic compounds containing atoms of oxygen, nitrogen, chlorine etc. are particularly interesting. Among the first semiconducting polymers, and the most thoroughly investigated, are the compounds obtained from poly(acrylonitrile)[21]. Published results[21-27] justify the conclusion that electrical conduction in pyrolysed poly(acrylonitrile) is determined by an ionic and an electronic contribution. The ionic contribution, which accounts for the conductivity of the initial polymer, is predominant in specimens prepared at 150–300°C, and decreases with increasing temperature of heat-treatment. At the same time the electronic contribution increases, as required by the increasing number of conjugated double bonds. The increase in electrical conductivity resulting from treatment at 400°C is due to an increase in the effective mobility of current carriers, not to an increase in carrier concentration. Studies of the temperature dependence of electrical conductivity and of thermoelectric power have led to the conclusion that the regions of polyconjugation in poly(acrylonitrile) specimens treated at low temperatures have the properties of impurity semiconductors, changing to semimetal properties as the temperature of heat-treatment is raised. The unpaired electrons which are manifest in the ESR spectra behave as donor impurities[28-30]. It has been shown that the value and the temperature dependence of the electrical conductivity are determined essentially by activated jumps between polyconjugated regions, whereas the thermoelectric power is characteristic of the polyconjugated regions themselves. Estimates of the carrier mobility give values of the order of 10^{-3} cm^2 V^{-1} s^{-1}. These results were obtained by assuming that the band theory can be applied to the system. Although the validity of the band model as applied to organic polymers is by no means established, experiment shows that the formalism of this model gives a fairly consistent picture of the mechanism of charge transfer when applied to poly(acrylonitrile). Work[31,32] on the effect of hydrostatic pressure and tension on the resistance and thermo-e.m.f. of poly(acrylonitrile) filaments is particularly interesting. It was shown that the concentration of free carriers remains constant on raising the pressure, whereas the activation energy of electrical conduction decreases. It follows that the change in conductivity with temperature is determined by the activated nature of the mobility and is associated with the height of the potential barriers separating the regions within which electrons are delocalised. Longitudinal extension increases the distance between molecules and should therefore increase the height of the potential barriers, lower the mobility of the current carriers, and increase the resistance, as is experimentally observed. Kustanovich and coworkers[33,34] have shown that the electrical properties of pyrolysed filaments of poly(acrylonitrile) are determined by gases adsorbed on the surface: this suggests that results obtained in the presence of air should be critically re-examined.

In principle, results obtained on pyrolysed polymers should be difficult to interpret because the structure of the resulting products is usually poorly characterised, and there can be no doubt that heat treatment leads to the appearance of new formations which behave as impurities and are difficult to control. In this context, it is interesting to note reports[35,36] of changes in the electrical properties of poly(acrylonitrile) under the influence of infrared radiation.

An extensive series of papers by Berlin and coworkers and by other authors is devoted to the electrical and magnetic properties of polymers containing acyclic conjugated systems (polyvinylenes)[37-46] and polymers with aromatic rings in the conjugated chain[47-56]. These workers examined the change of conductivity with temperature, and its relationship to paramagnetic absorption and to the structure of the polymer. Most of the polymers investigated had fairly high resistivities ($\sigma_d < 10^{-7}$ ohm^{-1} cm^{-1}) and gave an electronic paramagnetic absorption signal with a g-factor corresponding to the free electron. In spite of the considerable effort devoted to studies of the relationship between the ESR signal and the electrical properties of highly conjugated polymers[37-39,50-72], the relation between current carriers and the concentration of paramagnetic centres is still far from clear. Blyumenfel'd and Benderskii ascribe the ESR signal and the electrical conductivity to the formation of polar charge-transfer complexes either between two neighbouring molecules or by the trapping of charge at a crystal imperfection[57-64]. Another approach is based on the suggestion by Berlin[65-68] that high-molecular-weight fractions containing stable biradicals are formed during the synthesis or the subsequent heat treatment, and that these are the source of current carriers.

Many workers have studied the influence exerted on the semiconducting properties by polymer structure, both supermolecular (crystallinity, degree of order, etc.) and molecular (chemical structure of the macromolecule itself). As a rule, the electrical conductivity increases on increasing the number of π-electrons in the molecule and when atoms with electron-donating properties are introduced into the chain[73-77]. When groups or heteroatoms which interrupt the conjugation are introduced into the macromolecule, the electrical conductivity decreases as a result of the increased activation energy for conduction[50,53,78-84]. Experiments with poly(phenylacetylene) have shown that the activation energy for dark conduction is independent of the molecular weight and corresponds to the radiation maximum in the luminescence spectra[61,62]. This is evidence for the generation of carriers by thermal ionisation of luminescence centres.

However, the electrical properties of polymers depend not only on the degree of conjugation in the macromolecule but also on the physical structure of the polymer. Hatano and Kambara[85,86] found that the resistance of crystalline polyacetylene is lower than that of the amorphous material by 5–8 orders of magnitude. It should be noted, however, that the oxygen content was rigidly controlled in this work. The electrical properties of a series of chelate polymers were shown to be determined, in the first instance, by the degree of order in the polymer and by the nature of the electronic interactions, rather than by the structure of the individual macromolecule[87,88]. The conductivity can be raised by introducing into the macromolecule groups tending to make it more flexible and thus favouring denser packing[54,87,89,90]. Many workers have noted conduction anisotropy with respect to the alignment axis of the macromolecules[28,29,31,91,92], an increase in conductivity with pressure[93-95], and a major influence of adsorbed vapours and gases on the electrical conductance (particularly oxygen)[42,87,96-101]. The effect of oxygen on the electrical conductivity involves either a change in the concentration of current carriers or a modification of the height of the potential barriers between macromolecules or polyconjugation regions. Most high-resistance polymeric semiconductors show a linear dependence (compensation effect) of the activation energy E_d on the logarithm of the pre-expo-

nential factor σ_0 in Eqn. (1)[48,57,58,102,103]. Sazhin and coworkers[104-107] have studied the temperature dependence of electrical conductivity and its relationship to supermolecular structure on a series of polymeric dielectrics.

Compounds containing a metallocyclic ring in the main chain form an important group of semiconducting organic polymers. Poly(copper phthalocyanine) was synthesised by Epstein and Wildi[108-109]. The resistivity of the polymer at room temperature is 10 orders of magnitude lower than that of non-polymeric copper phthalocyanine (10^7–10^8 ohm cm). Interesting Hall effect measurements are reported in the same paper, from which valuable conclusions may be drawn as to the conduction mechanism. It is found that the change in resistance with temperature of a polyphthalocyanine which has not been heat treated reflects both a change in mobility and a change in the carrier concentration. The mobility value was 10 $cm^2\ V^{-1}\ s^{-1}$, and it is interesting to note that it was obtained by direct measurement (Hall effect). Indirect methods of measuring mobility in polymers usually yield values many orders of magnitude lower. Direct methods of measuring mobility (such as the transit-time method) also give low values in polymers (10^{-3}–10^{-4} $cm^2\ V^{-1}\ s^{-1}$)[110]. The Hall constant for polyphthalocyanine heat-treated at 450°C did not change with temperature, pointing to a constant carrier concentration. In this case the activation energy for electrical conduction can be identified with the mobility activation energy.

Berlin, Frankevich and others also investigated polyphthalocyanines[98,97,111-114]. They noted a strong effect from vacuum and oxygen treatment on the electrical properties of the samples, and proposed a method for measuring carrier mobility in polymers by simultaneously monitoring the desorbed acceptor molecules and the electrical conductivity of the polymer[96]. They find that copper polyphthalocyanine is an n-type semiconductor with a mobility of 10^{-2} $cm^2\ V^{-1}\ s^{-1}$ and a concentration of current carriers of 10^{18}–10^{19} cm^{-3}.

Polymeric chelate materials with semiconductor properties have been prepared also from tetracyanoethylene[115-127]. By measuring electrical conductivity at high frequencies it was found that the resistance and the activation energy for electrical conduction decrease with increase of frequency. Hence, the barriers between macromolecules must be taken into account when discussing the conduction mechanism[119-121]. Polymeric chelate compounds are among the most promising materials for technological applications. In polymers of the coordination type we can expect high mobilities and broadening of the energy levels into wide bands. Semiconducting chelate polymers have been prepared from ferrocene[16,48,128-131], poly(vinyl alcohol)[32] and other compounds[77,133-144].

A large group of semiconducting polymers consists of compounds with conjugated triple or cumulative bonds in the main chain[145-163]. A poly-yne with the appearance of a black powder containing 98% of carbon and retaining the structure of polyacetylene up to 200°C has been prepared and investigated[146,152,153]. The polymer shows n-type conduction, the donor centres being copper atoms included in the molecular carbon chain of the polyallene structure. On raising the temperature of heat treatment the polymer changes conductivity type, which the authors ascribe to thermal dissociation and removal of copper and hydrogen atoms from the carbon chain. Under these conditions the terminal carbon atoms behave as electron acceptors. Infrared and X-ray diffraction analysis[147-153] have shown that these carbonaceous products of acetylene condensation are open forms of carbon in which linear macromolecules with a poly-yne and partly a cumulene structure are aggregated in molecular packs of parallel carbon chains. Some of the macromolecules are "cross-linked" into a spatially disordered conjugated polyene structure. Studies of the electrical properties of poly-yne derivatives before and after heat treatment, in cases where the structure consists of parallel molecular chains aggregated into packs with a high degree of azimuthal order[148,149], have shown that these materials also are semiconductors.

Radiation-thermal treatment of polymers appears to be a promising method of preparing materials with semiconducting properties[92,164,165]. For example, the method has been used to prepare semiconducting materials from polyethylene[70,98,165-169], with conductivities between 10^{-14} and 10^2 $ohm^{-1}\ cm^{-1}$, activation energies for conduction between 0 and 1.5 eV, and thermoelectric power between 1 and 500 $\mu V\ deg^{-1}$. Ohm's law is obeyed up to fields of 10^3 V cm^{-1}. At the boundary between low-pressure polyethylene and polyethylene subjected to radiation-thermal treatment, p–n junctions have been obtained with a rectification ratio of 10 in the region of 400–600 mV[165]. The model adopted for the conduction mechanism involves polyconjugation regions 50–100 Å long alternating with barriers 5–20 Å thick which determine the activation energy of the conduction process[98]. Current rectification has been observed also at the junction between polyethylene crystals and metals[170].

The formation of charge-transfer complexes between a polymer and electron-donor molecules[98,102,168,169,171-185], resulting in an increase in conductivity by 4–6 orders of magnitude, offers very attractive possibilities for the preparation of low-resistance polymers. In addition to the compounds mentioned above, semiconducting materials which have been investigated include those prepared from poly(diphenyldiacetylene)[186], polypyrroles[187], polybutadiene[188], poly(azophenylenes)[189], polyaniline[190,191], poly(vinyl acetate)[192] and various other materials[103,193-199]. The semiconducting properties of organic polymers (in the dark) have been discussed in a number of review articles[16,99,102,200-208]. Lastly, we shall note that proteins and nucleic acids have been shown to have quite specific electrical properties of the semiconductor type in a number of investigations[209-224] which cannot be discussed in detail in the present article.

IV. PHOTO-SEMICONDUCTING PROPERTIES OF ORGANIC POLYMERS

Whereas studies of the electrical conductivity, thermoelectric power and ESR spectra of organic polymers are relatively abundant, reports of photoelectric phenomena in organic macromolecular compounds began to appear only during the past 5 years, and are far from numerous. We must stress that the study of photoelectric processes in polymers gives a fuller description of electronic phenomena in these systems than is available from studies of electrical conductivity, since a light beam allows us to probe strictly defined energy states of the electrons. Furthermore, the photo-semiconductors (which behave as insulants in the dark) become accessible to study. These materials are of interest in electrophotography—the only technological area in which organic photosemiconductors have yet found a genuine practical application. It is significant that the number of patents on electrophotographic layers made from organic materials is ever increasing. The patent literature dealing with this subject has been reviewed by Sidaravichyus[225] and by Newman[226,227]. The

most widely used electrophotographic layers are those of poly(vinylcarbazole). However, their physical parameters have been investigated and they have been found to be a hundred times less sensitive than such inorganic materials as selenium sensitised by zinc oxide[228-232]. On the other hand, they have a high resolution (absence of grain structure) and higher contrast than is found in selenium, they are unaffected by the material and size of the substrate, they are technologically attractive, and they offer a number of other advantages. The best promise of improving the sensitivity of organic polymer layers lies in the addition of chemical sensitisers[233] and in the search for new materials[234,235].

The formation of photoelectrically sensitive materials by u.v. irradiation of the copolymer of vinylidene chloride (85%) and vinyl chloride (15%), known as Saran Wrap, was first reported by Oster and coworkers[236,237]. The photoconductivity was attributed to the formation of free radicals under illumination because conditions which induce or eliminate the ESR signal affect the photoconductivity in the same sense. It should be noted that the preparation of polymeric materials with semiconducting properties by irradiation with monochromatic light has some important advantages over alternative methods such as pyrolysis: (1) by appropriate choice of wavelength, it is possible to initiate chemical reactions selectively; (2) the light beam can be confined to particular areas of the target. By virtue of these effects, Oster and coworkers were able to prepare p–n junctions at the interface between differently irradiated areas.

The search for photoelectrically sensitive polymers has been pursued by the present writer for many years in A. N. Terenin's laboratory. Approximately 400 organic polymers have been examined so far [poly(phthalocyanines), polyphenylenes, poly(cyanamides), poly(acetonitriles), polyferrocenes, poly(phenylacetylene) and its copolymers, polymers of malonic and adipic acid, stilbene polymers, poly(vinylphthalimides), polymers of quinizarine with metals, many different chelate polymers, etc.].

Some of these materials, when tested for d.c. photoconductivity, showed a small increase in conductivity with a slow relaxation when illuminated, but it was not possible to distinguish a photoelectric effect unambiguously from the bolometer effect.

By using the capacitor method of photo-e.m.f. measurement[238] with modulated light (300 Hz), polymers with a photocurrent relaxation time of 10^{-2} s were found, and the photoelectric processes in these compounds were examined in detail[100,239-252]. The polymers in question were compounds with triple bonds[239] and poly(metal acetylides)[240]. The compounds were synthesised in Korshak's laboratory by Sladkov and coworkers[145-154,253-256]. An internal photoeffect was observed in 50 of the 70 compounds examined, whose structure can be represented by the formulae

$$R'\!\left(-C\equiv C-R-C\equiv C-\right)_n R'; \quad R\left(-C\equiv C-\right)_n R,$$

where R and R′ are organic radicals containing functional groups or hetero-atoms. The polymers are finely divided powders of colour varying from white to black, poorly soluble or quite insoluble in organic solvents.

Under illumination, the capacitor photo-e.m.f. is observed in the u.v. or visible region of the spectrum[239,243]. In the most of the poly-ynes, the photocurrent carriers have a positive sign. Previous irradiation of the polymers with u.v. light has been shown to increase the photo-e.m.f. This effect is ascribed to ionisation of the conjugated molecules under the influence of u.v. light and formation of centres acting as traps for the photo-electrons. This mechanism is confirmed by some preliminary experiments by the ESR method[249,250]. With poly(pp'-diethynylazobenzene) at 77°K, a partially reversible ESR signal photo-induced by u.v. light can be observed. By comparing the behaviour of the ESR signal with that of the photo-e.m.f. under u.v. light we conclude that the photo-induced ESR signal is due to the capture of photoelectrons by the positively charged local centres formed in the polymer structure by the action of u.v. light. The spectral distribution of photo-e.m.f., measured on a number of polymers, is characterised by smoothly increasing curves (towards higher energies) with a threshold at 2.0 eV.

The dark resistance of the poly-ynes is 10^{12}–10^{14} ohms, decreasing by 2–3 orders of magnitude under the light of a mercury lamp[242,249]. The variation of the photocurrent i_{ph} with illumination (L) is of the form $i_{ph} = \alpha L^n$, where n can vary between 0.5 and 1.0. The photocurrent is proportional to the voltage raised to the power n, where $n > 1$. A typical range of relaxation times for the photocurrent in poly-ynes is between 10^{-5} s and several seconds. From the initial rise and decay of the photocurrent we can extract an exponential component with a time constant of approximately 10^{-5} s.[241] We should stress that poly-ynes and polyacetylides are the only polymers for which such short-lifetime photoconduction processes have yet been reported. With time constants of this order there can be no doubt that the photo-effect in these polymers is electronic in nature. After the initial exponential stage, the relaxation of photoconductivity changes to a hyperbolic law in a time interval of between 10^{-5} s and several seconds[241].

As for the photo-e.m.f., the spectral distribution of the photoconductivity in poly-ynes and of the influence of u.v. light on these materials was investigated[242]. The photoconductivity spectra are displaced towards longer wavelengths as compared with the photo-e.m.f. spectra. The main photoconductivity maximum for poly(pp'-diethynylbenzene) is found, as in most other photoelectrically sensitive semiconductors, beyond the edge of the absorption curve, pointing to a difference between the rates of surface and volume recombination of the photocurrent carriers. The activation energy for poly(pp'-diethynylazobenzene), measured from the photoconductivity spectrum, was 1.82 ± 0.02 eV. The same value was recently obtained in Japan for the activation energy of dark conduction in this polymer[162]: this suggests that the same electronic transitions are responsible for both the dark conduction and the photoconduction in the polymers. As with the photo-e.m.f., the photosensitivity of poly-ynes undergoes a partially reversible change under the influence of u.v. light. Spectrally [with poly(pp'-diethynylazobenzene), say] this change consists in a redistribution of the ratios of the intensity maxima in the photoconductivity spectrum and a shift towards longer wavelengths of the short-wavelength maximum. The change in photoconductivity under u.v. irradiation, like the change in photo-e.m.f., is associated with the capture of the photoionisation electrons by the resulting traps, as shown by the ESR measurements discussed above.

Using the copolymer of p-diethynylbenzene and p'-nitrophenylacetylene, the absorption spectra in solution and in thin film form have been compared with the photoconductivity spectra. Photoconduction is observed in the absorption band of the polymer, and its trend is similar to that of the absorption spectrum[243].

A photoeffect has been found in 15 poly(metal acetylides)[240,250] having a chain structure expressed by the general formulae R–C≡C–M and M–C≡C–R–C≡C–M,

where R is an organic radical and M is a metal (Cu, Ag). Most of the work was done on copper derivatives, and in particular on poly(copper phenylacetylide), abbreviated CPA. These polymers are insoluble, fine powders of different colours, from yellow to dark red, and are coordination compounds[245]. The poly(copper acetylides) had a resistance of 10^9–10^{10} ohm in the dark, decreasing to 10^7–10^8 ohm on illumination with monochromatic light. Growth of the photocurrent to the steady-state value was accomplished in 10–15 s. As with the poly-ynes, the variation of the photocurrent with illumination is given by the formula $i_{ph} = \alpha L^n$, where n varies between 0.5 and 1. Ohm's law is obeyed up to fields of 10^2 V cm^{-1}, beyond which the photocurrent increases faster than linearly with applied voltage. The sign of the photocurrent carriers in all the poly(copper acetylides) is positive[240].

A comprehensive study of the spectral distribution of photo-e.m.f., photoconductivity, absorption, and luminescence in CPA has been described[245]. The photo-e.m.f. spectrum was found to be similar to the absorption spectrum, but the photoconductivity spectrum is displaced towards the long-wave region as compared with the others and has a maximum beyond the absorption edge. The latter fact denotes an important contribution from surface recombination of the carriers, arising from an extensive system of surface states. The increase in photo-e.m.f., accompanied by a decrease in luminescence yield, due to previous illumination, was investigated spectrometrically but remains puzzling.

Work done so far justifies the assumption that the absorption, photoeffect, and luminescence maxima in CPA are similar in nature. The bands are characteristic of fundamental electronic transitions in the polymer. Migration of charge carriers in CPA is assisted by the lowering of the potential barriers between molecules caused by π-complex bridging between the electron-acceptor copper atoms and the acetylene bonds. Changes in the luminescence and photoeffect spectra under u.v. irradiation are due to the rupture of weak coordination bonds in the polymer, which alters the relationship between polymer homologues. Bond breaking facilitates the dissociation of excitons at the resulting defects, leading to an enhanced photoeffect and a lower luminescence yield. This mechanism is supported by numerous experiments on the luminescence of CPA at 77°K[245], in which it was shown by spectroscopic measurements that the degradation of CPA under u.v. light proceeds up to the stage of formation of isolated molecules of diphenylbutadiyne dispersed throughout the polymer structure. Under these conditions we may postulate energy transfer from the semiconducting substrate (CPA) to the diphenylbutadiyne molecules.

Vapours and gases can strongly affect the semiconductor properties of polyacetylides[100,244]. Dry oxygen produces a reversible decrease in the electrical conductivity and photoconductivity by 3–2 orders of magnitude, and lowers the photo-e.m.f. by a factor of 3–5, which is unusual for a p-type semiconductor such as CPA. Gas adsorption on a semiconductor surface may lead, in the first instance, to the formation of a double layer resulting from the adsorbed molecules, and secondly to the creation of new recombination centres or trapping levels. An investigation of the effect of oxygen on the spectral distribution of photosensitivity has identified the quenching effect of oxygen with the formation of effective recombination centres which decrease the lifetime of majority carriers (holes). The recombination centres created by oxygen are primarily surface states, as shown by special experiments on the effect of u.v. light in vacuum, in which it was found that oxygen is photodesorbed from the CPA surface in a vacuum[100,248].

Water vapour reversibly suppresses the electrical conductivity and photoconductivity, and enhances the photo-e.m.f. of CPA[244]. The effect of water vapour on the photosensitivity spectrum has been examined, and shown to be associated with the formation (following adsorption) of an electrical double layer on the CPA surface, resulting from capture of the majority carriers (holes) on surface states.

Electron-acceptor molecules such as quinone and chloranil in the gas phase did not appreciably affect the photo-e.m.f., but suppressed the photoconductivity and the conductivity of CPA[249]. When the specimen was exposed to these molecules in solution, the photo-e.m.f. increased by an order of magnitude but its spectrum did not change appreciably. Evidently, new centres are formed by contact with the solvent, and these enable the quinone molecules to be adsorbed and act as electron traps owing to their high electron affinity. The presence of highly developed surface states, indicated by the above results on the effect of gases and vapours on the electrical properties of CPA, implies catalytic activity towards oxidation reactions[251].

From the view point of applying the concepts of semiconductor physics to biological polymers, some curious results have been obtained in a study[252] of the effect of nucleic acids and amino-acids on the photosemiconducting properties of CPA. In particular, it was shown that deoxyribonucleic acid and ribonucleic acid increase the conductivity and photoconductivity of the polymer by 2–3 orders of magnitude without affecting the spectral sensitivity. The photo-e.m.f. is increased several-fold. An investigation of the effect of purine and pyrimidine bases, which enter into the composition of nucleic acids, showed that only adenine exhibits the effect. The mechanism of these phenomena is probably similar to the process which has been termed chemical sensitisation in inorganic semiconductors[257]. It should be noted that studies of the interactions between biological polymers and model synthetic polymers have opened up new pathways for investigating the specific biological properties of these compounds.

The mechanism of the photoeffect in polymers is probably as follows. The primary act consists in the excitation of a molecule by the absorption of a photon[239,249,250]. The excited state (or exciton) migrates until it collides with a structural or chemical defect, on which a pair of free photocurrent carriers is formed. The electron is retained by the positively charged centres, but free holes can migrate through the entire system of macromolecules. In CPA it would appear that pair formation does not require an activation energy, as shown by the temperature dependence of the photoconductivity at very high frequencies[258]. Potential barriers at the boundaries between macromolecules can be expected to limit the photoelectric sensitivity of the material very markedly. Hence the role of random bonds associated with cross-linking of the macromolecules becomes important.

An effect not previously observed in organic semiconductors—the spectral sensitisation of the photoeffect by dyes—has been found and spectroscopically investigated in poly-ynes and polyacetylides[246–250]. The effect is well known in inorganic semiconductors[259,260], and consists in the appearance of photoelectric sensitivity in the absorption band of a dye adsorbed on the surface of a photoconductor. The sensitisers used in conjunction with poly-ynes and polyacetylides include Methylene Blue, Pinacyanol, chlorophyll, phthalocyanines, erythrosine, hematin, Rho-

damine B and others. The sensitised photoconductivity spectrum and photo-e.m.f. spectrum are similar to the absorption spectrum of the dye in solution (10^{-3} M), which suggests that the monomeric form of the dye takes part in the sensitising act. Dimers and more highly aggregated forms of the dye also take part in the sensitising process. Because of the influence of adsorption forces, the sensitised photosensitivity spectra are displaced by 10–15 nm as compared with the absorption spectra of the dyes. The effectiveness of spectral sensitisation can be as much as 30–40% of the intrinsic photoelectric sensitivity. Adsorption of the dye alters the intrinsic photoelectric sensitivity of the polymeric substrate. For example, the intrinsic photo-e.m.f. was increased by a factor of 30 by adsorption of erythrosine. A detailed study of the spectral curves for intrinsic and sensitised photoeffects (photoconductivity and photo-e.m.f.) has been made using Methylene Blue, chlorophyll *a*, and Pinacyanol. With Methylene Blue it was shown, by a spectrometric method, that the efficiency of spectral sensitisation is a maximum at a solution concentration of the dye of 10^{-3} M. The sign of the photocurrent carriers is the same in the intrinsic and in the sensitised region. The results indicate that the sensitised photoeffect in organic semiconductors follows the same pattern as in inorganic semiconductors. Dyestuffs of the most diverse classes—strong electron acceptors such as Methylene Blue, and readily oxidised compounds such as chlorophyll—are equally effective in sensitising the photoeffect in organic semiconductors. Dyes of the following types are found to act as sensitisers: cationic (Pinacyanol, Methylene Blue), anionic (erythrosine), and neutral (chlorophyll, phthalocyanine, hematin), some of which belong to the photographic sensitiser class (Pinacyanol) and others to the desensitiser class (Methylene Blue). As with inorganic semiconductors, sensitisation occurs through the monomeric, dimeric, and higher polymeric forms of the dye. Some of the dyes examined as sensitisers do not themselves show photoelectric sensitivity in the solid phase, but those that are photoelectrically sensitive show a large increase on adsorption. Therefore, the most likely sensitisation mechanism involves energy transfer from an excited dye molecule to electrons in the filled band or on levels close to it and promotion of these electrons to empty traps, thus promoting the free motion of positive holes. Data obtained from ESR and data on the influence of vapours and gases on the photoelectric properties of polymers suggest that these localised traps are mainly on the surface. The observed change in the intrinsic photoelectric sensitivity of the polymer is related to the nature of the traps generated by the adsorbed dye.

The phenomenon of chemical and spectral sensitisation of the photoeffect, recently described for poly(vinylcarbazole)[261] and polyacenaphthylene[262], is analogous to that found in polyacetylenes. The high photoelectric sensitivity of poly-ynes and polyacetylides has enabled these materials to be made into electrophotographic layers of sensitivity comparable to that of inorganic photosemiconductors[234].

Bradley and Hammes[263,264] have reported photoconductivity in thin (~ 1 μm) organic layers produced by polymerisation in the glow discharge of monomers containing nitrogen, sulphur, selenium, and certain metals. Irradiation with unfiltered white light raised the room-temperature dark conductivity (which was of the order of 10^{-17}–10^{-13} ohm^{-1} cm^{-1}) by a factor of 10^3. The activation energy for photoconduction in these films is 0.25 eV, pointing to thermal activation with formation of free carriers from excited molecules in an intermediate, non-conducting state, rather than band-to-band transitions. All the polymers gave short-circuit photocurrents, evidently due to a photovoltaic effect at the interface between the film and the transparent electrode. The charge carriers were identified as electrons from the polarity of the photocurrent.

It is interesting to note that addition of a trace of iodine during polymerisation in the discharge increased the electrical conductivity and photoconductivity by three orders of magnitude. The authors point out that their results are characteristic of amorphous organic semiconductors in general rather than of any specific polymer structure. The importance of this observation is obvious if we remember that the authors did not control the composition or the structure of their films, produced by polymerisation in a discharge. Clearly, it is impossible to discuss the observed semiconducting properties in terms of the structural parameters of the macromolecule or of the sample as a whole. However, systems of this type can already be of practical interest. For example, these films have been used successfully as high-temperature photodetectors (up to 200°C).

Rozenshtein, Davydov, and others observed photoconductivity in polymeric Schiff's bases made from benzil and *p*-phenylenediamine[265], polyazines[266,267], and poly(diphenyldiacetylenes)[268]. The activation energy for photoconduction in these compounds was shown to lie between 0.1 and 0.3 eV. With poly(diphenyldiacetylene) the activation energy for photoconduction was found to increase with wavelength of the light, due to the existence of an energy distribution of trapping levels. The intensity–current characteristic is of the usual form ($i_{ph} = \alpha L^n$), with n lying between 0.5 and 1. Ohm's law is obeyed up to field intensities of 10^2–10^3 V cm^{-1}. All the polymers have a resistivity higher than 10^{12} ohm cm in the dark. The poly(Schiff's base) gave appreciable photopolymerisation effects, making the interpretation of results difficult.

Drabkin and Rozenshtein proposed the use of the photoconductivity method to investigate changes taking place during heat treatment of polyacrylonitrile[269]. By comparing the time–temperature curves for the increase in the number of conjugated bonds with those for the photoconductivity the authors were able to show that the formation of conjugated bonds is a sufficient condition for the onset of electronic conduction on the polymer. However, it has been stated[36] that photoconductivity in polyacrylonitrile is possible even without conjugated bonds. In particular, photoconductivity was demonstrated in a complex between the polymer (not heat treated) and dimethylformamide solvent. These results point to the need for careful removal of the last traces of solvent from polymer films before attempting to examine the films. The many conflicting data reported by different workers on the semiconducting properties of the same material may be due to varying specimen purity. On the other hand, the formation of charge-transfer complexes between donor-acceptor molecules and polymers is a very promising way of lowering the resistance of polymeric materials and increasing their photosensitivity[180–184,233,270,300].

A group of workers have synthesised poly [1,3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline][271] and polyacenaphthyls and their nitrile derivatives[272], and studied their photoconductivity. The photoconductivity spectrum of the first polymer[271] is reported in the region from 300 to 600 nm. The superlinear law relating the photocurrent to illumination ($n = 1.2$) reported by these workers is unusual in organic semiconductors. Some of the polymers examined have proved useful in electrophotography.

A report by Drechsell and Görlich[273] of photoelectric sensitivity in a polyvinylene film, prepared from poly-(vinyl alcohol) by elimination of water in the presence of dehydrating agents, is noteworthy. The Hall constant of the resulting material was measured, and used to calculate the carrier density (of the order of 10^{16} cm^{-3}) and mobility (10^{-3} cm^2 V^{-1} s^{-1}). The conductivity type was electronic. This polymer is of interest primarily as a possible infrared detector, since photoconductivity occurs in the region of 0.6–6.4 μm according to the photoconductivity spectrum published by the authors. Mrosowski and coworkers[274,275] had previously suggested the possible use of pyrolysed films of cellophane or poly(acrylonitrile) as infrared detectors. However, their results do not show unequivocally that the observed effect was not bolometric.

Beck[101] discusses the photoconductivity of polyphenylene and polyvinylenes. At room temperature, and depending on the polymerisation conditions and on the oxygen content, the observed resistivities fell in the range 10^{1}–10^{15} ohm cm, with activation energies between 0.025 and 0.96 eV. A small decrease in resistance was observed in the unfiltered light of a filament lamp. In the discussion of the kinetics of the photocurrent the author distinguishes between a primary (fast increase in photocurrent with time of irradiation) and a secondary photoeffect (long-term increase in photocurrent). According to Beck, the primary photoeffect corresponds to the $^0E \rightarrow {}^1E$ transition, and the secondary photoeffect to the $^1E \rightarrow {}^3E$ transition, where ^0E is the ground state of the molecule, ^1E is an excited singlet state, and ^3E is a triplet state of the molecule. This distinction is evidently unjustified, since there are no grounds for identifying the excited state of the molecule with the state giving rise to conductivity. Even less justified is the conclusion that the secondary photocurrent is associated with a triplet state of the molecule. The so-called secondary photocurrent is due, in all probability, to the physical condition of the polymer and to defective contacts. Beck[101] proposes a tunnel mechanism for the transition across molecular potential barriers, and gives an estimate of 0.6 cm^2 V^{-1} s^{-1} for the carrier mobility.

A photoeffect has been observed in polyethylene under the action of u.v. light[276,277]. The quasi-classical method of calculation of the ionisation potential of polyethylene in the solid state gives a value of 4.5 eV. Absorption spectral studies revealed the presence of structural and impurity absorption, but no threshold was found in the region of 4.5 eV. The observed photo-e.m.f. and photoconductivity are probably due to impurities, and further work is needed to explain the nature of charge carriers and traps in this material. The mechanism of formation of free charges in polyethylene is likened to charge separation in an assembly of n–p–n structures connected in series. The extent to which such a mechanism can be justified is not yet clear. We note that photoconductivity has been observed also in the radiation-thermal treatment products of polyethylene[167,278].

Photoelectric sensitivity in biological polymers has been observed in an extensive series of investigations[221,224,279-282]. Liang and Scalco observed photoconductivity in adenosine[279], in the sodium salt of deoxyribonucleic acid[280,281], and in polyglycine[286]. The sodium salt of deoxyribonucleic acid had an anomalously high thermal activation energy for photoconduction, 0.9 eV, as compared with the values commonly observed in organic semiconductors. The authors ascribe the high activation energy for photoconduction to the existence of two contributions: (1) the energy required to generate free carriers, and (2) the energy which the carrier must have in order to overcome the potential barriers opposing its motion. We should note that the light source used by these workers—a tungsten filament lamp—had an energy maximum at about 1 μm, whereas the materials examined have an absorption maximum in the u.v. region, showing that the observed photoconduction is due to impurities. The nature of the photoconductivity (whether ionic or electronic) has also not been finally established. Nelson[221] observed photoconductivity in hemoglobin and in gelatin stained with dyes. He suggested that, following light absorption by the protein, energy is transferred by a radiationless resonance mechanism to the dye, which acts as the most easily ionised centre. Studies of photoelectric phenomena in biologically important polymers are only just beginning, and they cannot fail to yield important information on the properties of these polymers in the near future. The writer believes that combined investigations of the photoeffect and luminescence in these compounds will be the most valuable in this field.

A decrease of resistance under illumination is reported in a number of papers dealing with organic polymers, besides those mentioned above. The phenomenon is mentioned in the case of polyacene quinone polymeric radicals[73], poly(*p*-diethynylbenzene)[156], chelate polymers[88], polyazopolyarenes[283], poly(tetrafluorethylene) irradiated by X-rays[284], and others[285]. Extremely interesting work has been reported also on the photoelectric sensitivity of polydisperse organic systems with dyes in the polymer matrix[286,287], or inorganic ions and semiconductors[288].

V. CONCLUSIONS AND PROSPECTS

The vast fund of data on the electrical phenomena taking place in organic polymeric semiconductors, accumulated during the past 5–8 years, is indicative of the rapid development of this branch of knowledge. It must be admitted, that serious obstacles exist to further scientific progress and to the large-scale penetration of these materials into technology. From the scientific point of view these difficulties arise primarily from our uncertain knowledge of the structure of most of the materials examined. This is specially true of polymers prepared by pyrolysis, radiolysis, and similar methods. During the modification of the starting polymers by these methods, far-reaching structural changes undoubtedly occur. Yet, only very few papers deal with the structure of the macromolecule and with the physical structure of the final product. As a rule, authors confine themselves to a statement that their materials have a heterogeneous structure with polyconjugation regions separated by unspecified barriers. Views regarding the size, crystallinity, degree of packing etc. of these formations are extremely hazy. In spite of this, far-reaching conclusions are drawn as to the relationship between the chemical structure of one macromolecule and the electrical properties of the polymer as a whole: in these circumstances, such conclusions are hard to justify. It should be noted that even attempts to correlate the semiconductor properties of low-molecular organic semiconductors (dyes) with the specific chemical structure of their molecules have encountered serious difficulties[289,290]. It is now well established that supermolecular structure is the decisive factor which determines the specific photosemiconducting properties of dyes, whereas the molecular structure (presence of π-electrons) leads only in principle to the appearance of semiconductor properties[9,10,291].

The position is slightly more favourable with polymers prepared by direct synthesis, since in most cases the

chemical structure of the macromolecule is accurately known. But even with these materials the inadequacy of the information as to the role of the physical structure of the resulting polymers in determining their semiconducting properties is readily apparent. Little is known of the influence of defects and foreign impurities on the semiconducting properties of organic polymers. Inorganic semiconductor materials with prescribed properties became available only by rigorous purification followed by doping with the correct impurities. Some problems in solid-state electronics have been solved only by preparing inorganic semiconductors with a total impurity content of 10^{-9}–10^{-10}%. With organic semiconductors, the figure (in the most favourable cases) is higher by 8–9 orders of magnitude.

Thus, whilst not denying the value of a search for new semiconducting organic polymers, the writer believes that there is an urgent need for more detailed studies of their specific physical structure from the point of view of solid-state properties. It is obvious in principle that a periodic chain consisting of carbon atoms attached to an equal number of hydrogen atoms must have an electronic spectrum with allowed and forbidden energy bands. If hydrogen atoms in the chain are replaced by side-groups, the latter can play the part of impurities. Electropositive or electronegative substituents can be treated as acceptor or donor impurities respectively. In contrast to covalent crystals, in which impurity atoms can take up or give up one or several electrons, fixation or emission of a fractional electronic charge is possible in our systems. Transfer of a complete charge may require the cooperation of several bonds acting in the same sense. Many defects of various kinds, found in polymers, can also play the part of donor or acceptor impurities.

As the previous discussion shows, there are essentially two possible charge-transfer mechanisms: the hopping (or jumping) mechanism and the band mechanism. The low mobility values in polymers are a strong argument [292-297] in favour of the former mechanism, which consists of a series of consecutive, activated jumps by the current carriers from one macromolecule to the next. The activation energy for conduction in this case defines the probability of these jumps, and a temperature rise may be thought to increase either the effective mobility or the effective concentration of the current carriers. If the energy barriers are sufficiently permeable, there is also a finite probability of non-activated tunnelling transition by the electrons. According to theoretical work, the hopping mechanism is in principle incompatible with observation of the Hall effect: this may be the reason for the many failures to detect a Hall effect in polymers.

The band model assumes that the charge carriers move in generalised energy bands available to all the π-electrons in the polymer. The width of these bands decreases as the overlap of the wave functions of the π-electrons decreases, and in the limit the bands shrink to conduction energy levels or, in the terminology of the band model, to a very large effective mass of the charge carriers. The band model is based on the strict periodicity of crystalline materials, with allowance for the potential of a real crystal in determining the effective mass of the current carriers. However, many of the polymers in question are amorphous or largely heterogeneous materials. Thus a great deal of interest attaches to the possible application to these systems of the theory of liquid and amorphous semiconductors, in which the electronic properties are determined by short-range rather than by long-range order [296,297]. It has been shown on more than one occasion that long-range order is a sufficient but certainly not a necessary condition for the formation of energy bands [296,297].

Useful results have been obtained also by combining the ideas of the hopping and the band mechanism when dealing with the heterogeneous structures of organic semiconducting polymers. The band model is applicable to an individual macromolecule or to the polyconjugation regions, since these are strictly regular systems, and the conduction electrons can be treated as perfectly free. On the other hand, the migration of charge carriers between macromolecules or regions of polyconjugation is best described by the hopping mechanism.

Pohl introduced the concept of eka-conjugation [73,74] to describe a type of electron delocalisation for which even at room temperature the number of excited states is considerable. He estimates that eka-conjugation will appear if 10–15 pairs of conjugated bonds are present. The nature of the excited states is discussed in terms of excitons and ion–exciton complexes, mutually interacting, and thus substantially assisting the transfer of charge carriers.

In any case, we must remember that the number of organic semiconducting polymers is already of the order of one thousand, and is increasing all the time. It is obviously unreasonable to expect a single theory of electrical conduction to apply equally well to them all.

The problem of the generation of photocurrent carriers in organic polymeric semiconductors is also not finally resolved. By analogy with low-molecular organic semiconductors [1-8,60,64], the photoeffect is assumed to be a multi-stage process [239,248,249]. The primary step is the formation of a singlet or a triplet molecular exciton. These excitons give rise to transfer excitons (two ions) or to a free pair of carriers, either spontaneously or by interaction with defects or other excitons. The latter process depends on the relative contribution of the hopping and the band conduction mechanism. Direct optical transitions to conduction states are improbable under these conditions, which explains the absence of these particular bands in the absorption spectra of the condensed phase.

In addition to an increased concentration of current carriers, envisaged in the above mechanism of carrier generation, we can assume in principle that the role of light is to lower the potential barriers between individual macromolecules or polyconjugation regions. As a result, the effective conductivity increases. This mechanism may operate in polymers whose carrier concentration is unequivocally temperature-independent. The formation of non-equilibrium carriers can also lead to a lowering of the barriers through their polarisation effect. Both processes (increase in concentration and change of barrier height) will then operate together. It should be noted that a detailed analysis of the mechanism of photocurrent generation in semiconducting polymers is complicated by the insolubility (or poor solubility) of most of the compounds examined. Thus, the absorption spectra of the individual macromolecules (in solution) cannot be compared with the absorption spectra and photoeffect of polymers of uniform molecular weight in the condensed phase, which would offer valuable information on collective interactions in polymeric semiconductors. Hence, the development of synthetic routes to soluble semiconducting polymers is a problem of the first importance. At the same time, this approach would clarify the role of intercrystalline and other defective layers, which at present have a major effect on the results since much of the work has been done on compressed discs or powders. There is little doubt also that the availability of soluble polymeric semiconductors would have important repercussions in thin-film electronics.

In general, the problems involved in the practical application of organic semiconductors are of interest for their own sake, and much could be written about them. We wish to state the following. When organic polymers were first introduced into electronics, their basic role was that of insulators. With the appearance of semiconducting polymers, these materials are now considered as potential technological material for semiconductor electronics. Furthermore, the problem of developing materials showing superconducting properties at room temperature[298,299] on the basis of conjugated systems has now been formulated and is being studied. This broad field of applications for polymeric materials is not fortuitous: it derives from the extreme variety of their physicochemical properties and of the methods available for modifying them. Whilst the superconductivity concept has met serious objections, both experimental and theoretical, and needs to be extensively reconsidered, there can be no doubt about the application of semiconducting polymers. The first steps in this direction have already been taken with the preparation of electrophotographic layers[225-234]. Their main shortcoming at the moment is a relatively low photosensitivity, but as was mentioned above there are some effective methods of raising the sensitivity by introducing chemical and spectroscopic sensitisers into the polymers. Radiation detection from the vacuum u.v. to the far infrared becomes possible in principle by using these systems.

The position as regards the application of organic semiconductors is reminiscent of the 1920-1930's, when practical uses for inorganic semiconductors were first suggested. It should not be forgotten that almost 30 years had to elapse before inorganic semiconductors could make an impact on technology over a broad front, whereas studies of organic polymeric semiconductors go back less than 10 years.

Also, there is a tendency to use organic semiconductors as a direct replacement for inorganic semiconductors. In view of the specific properties of the organic materials, this is not always the best approach. Thus, we know that the most successful uses of inorganic semiconductors (in transistors, detectors of various kinds, etc.) depend on the high mobility of charge carriers which characterises these materials. Organic semiconductors, on the other hand, are inferior in this respect. Hence, we must look for specialised areas of application. One possibility is in the electronics of low currents. In organic semiconductors, non-linearity of the current–voltage characteristics sets in at relatively low fields (10^2–10^3 V cm^{-1}), and the materials can be used as non-linear elements (rectifiers, varistors, thermistors, etc.). In conjunction with photochemical methods, they can be used to develop new printing processes. A valuable property of these materials is their ability to transmit excitation, which may find application in entirely new systems of information transmission. As the nature of elementary processes in organic semiconductors becomes clearer, we can look forward to a better understanding of various facets of physical processes in living organisms (mechanism of photosynthesis, energy migration and storage processes in biological systems, carcinogenic activity, catalysis by ferments, colour vision, etc.).

The main problem in the physics and chemistry of organic polymeric semiconductors is the preparation of materials with prescribed electrical properties. Recent advances in polymer synthesis, and the use of newer and more rational physical methods of structure modification, justify the hope that the problem will be solved. There can be no doubt that, as our understanding of electronic processes in organic polymeric semiconductors becomes deeper, ever-widening fields of application in science and technology will be discovered.

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Precipitation Chromatography

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CONTENTS

I.	Introduction	39
II.	Brief historical outline	39
III.	Precipitation-chromatographic media	40
IV.	Precipitation-chromatographic methods of separation	41
V.	Diffusional precipitation chromatography	42
VI.	Theory of precipitation chromatography	43
	1. Problems of precipitation sorption	43
	2. Conditions for the formation of precipitation chromatograms	44
	3. Structure of precipitation chromatograms	44
	4. Quantitative analysis by precipitation chromatography	45
	5. Secondary phenomena	46
	6. Theory of diffusional precipitation chromatography	46
VII.	Applications of the method	47

I. INTRODUCTION

In most cases the usual sorbents do not exhibit high selectivity with respect to substances (ions) which do not differ markedly in their properties. The combination of ion-exchange or other chromatographic methods with the phenomenon of complex-formation in solution proved extremely useful and led to the discovery of many new efficient procedures for the separation of substances. This is also the idea of precipitation chromatography, which is based on another powerful chemical interaction, the formation of sparingly soluble compounds, in combination with the usual chromatographic methods. The introduction into the chromatographic medium of suitable precipitants as well as complex-forming agents permits selective and very rigorous control of the behaviour of the individual components of mixtures in their separation. The wide possibilities in choice of precipitants, including complex-forming precipitants, make precipitation chromatography one of the most universal methods in chemistry.

A fairly large number of published studies, has accumulated, in which the principles of precipitation chromatography were used. However, the literature on this problem is widely scattered and has been little systematised, and this retards the development and improvement of the method which is essentially very promising. In most monographs on chromatography, precipitation chromatography is either not mentioned at all (although a number of studies using essentially this method is often noted[1-3]) or the method is described very briefly purely on the basis of the paper by Gapon and Gapon (1948).[4-6] The textbook of chromatography published in Poland is an exception[7]: in the chapter devoted to precipitation chromatography 33 papers are quoted, and demonstrate the extremely wide variety of applications of this method. The special monograph of Ol'shanova et al.[8], the only one so far, mentions only about 60 papers on precipitation chromatography. A few more references are quoted in the thorough review on hydrolytic and precipitation chromatography by Hayek[9], but the selection of papers appears somewhat one-sided, as a result of which a number of very interesting developments in the method are not brought to the notice of the investigator.

In view of the existing situation in this field, the author thought it useful to include, together with a review of the basic principles and trends in the development of precipitation chromatography, a scientific and patent bibliography as complete as possible.

II. BRIEF HISTORICAL OUTLINE

The first known study involving elements of precipitation chromatography is in all probability that of Runge[10]. With purely decorative aims, he carried out chemical colour reactions (including reactions with formation of precipitates), by treating with salt solutions filter paper impregnated with various substances. Runge published his own work in 1855 as an album of novel paper chromatograms.

Tsvet[11], the founder of the chromatographic method, noted in 1906 and in 1910 that in many cases of the Schönbein–Goppelsroeder[12] "capillary analysis", put forward in 1861, the formation of a chromatogram on impregnating papers with pigment solutions can be accounted for by the precipitation of the pigment as a result of a concentration gradient of alcohol in the solvent (due to evaporation of the alcohol). However, since precipitation from solutions in these experiments is not caused by the formation of a new substance by a chemical reaction, Goppelsroeder's "capillary" chromatograms cannot be classified as precipitation chromatograms in the generally accepted modern sense of this term (see below). On the other hand, one would be fully justified in classifying as precipitation-chromatographic many reactions carried out in spot analysis[13], particularly in the "fractional" method of analysis which Tananaev proposed in 1920.[14] There are many studies in this field.

For a long time the application of the principles of precipitation-chromatographic separation was only desultory. A certain breakthrough took place in the 1930's. At the beginning of the 1930's Tsvet's chromatographic method was revived, but it was used as before for the separation of organic and biological substances. Towards the end of the 1930's Schwab and coworkers[15,16] suggested that the method be applied also in inorganic chemistry and used alumina extensively as sorbent for this purpose. It was then noted[16-19] that the sorption of certain inorganic ions on alumina exhibits the features (at least partially) of precipitation sorption. Then, following Flood's suggestion[20], paper impregnated with aluminium or chromium hydroxide

began to be used in the analysis of heavy metals[21-27]. The work of Erlenmeyer and coworkers[28-30] stimulated the use as chemical sorbents of organic substances such as hydroxyquinoline, dimethylglyoxime, etc., which form insoluble complexes with many metals[31-36].

In 1948 precipitation chromatography was formulated as an independent chromatographic method. The credit for this is deservedly given to the Soviet physical chemist Gapon. Together with his coworkers, he introduced precipitation chromatography as one of the classified varieties of the chromatographic method[37,38], formulated the basic principles of the precipitation-chromatographic separation of substances[39], and began the first systematic studies in this field[40-46]. Immediately after the appearance of the first fundamental paper by Gapon and Gapon[39], a considerable increase in publications on precipitation chromatography took place both in the Soviet Union and abroad. Starting with 1953, the number of annual publications is not less than 15–20.

III. PRECIPITATION-CHROMATOGRAPHIC MEDIA

In order to separate substances by the precipitation-chromatographic method, a substance capable of reacting with them (or with some of them) to form sparingly soluble reaction products is introduced into the solid phase in the chromatographic medium. Such a substance or ion is called the precipitant. However, the main bulk of the solid phase usually consists of the "carrier". The functions of the latter include imparting the necessary filtering capacity to the system and localisation in the solid phase both of the precipitant and the precipitates produced.

Carriers. Various sorbents (ion exchanger, molecular sorbents) are usually employed as carriers. Frequently solids which are completely inert chemically and physicochemically are also employed as carriers; they serve as fillers, which are introduced mainly to improve the hydrodynamic conditions. In this case powders of sparingly soluble inorganic or organic substances, for example zinc sulphide, dimethylglyoxime, and hydroxyquinoline are used as precipitants. The powdered carriers and sparingly soluble precipitants usually have an average degree of dispersion equivalent to diameters of 0.01–0.1 mm.

The sorbent-carriers retain the precipitates in the form of ions (on ion-exchange resins, zeolites, alumina, and other exchangers), molecules (for example, various organic bases on activated charcoal[47]), or even colloidal particles (for example, the colloidal precipitate of aluminium hydroxide on filter paper[21-27]). One of the principal requirements which must be met by sorbent carriers is also that the carriers should retain the reaction products (precipitates) as well.

In column precipitation chromatography the following carriers are usually employed: alumina ("anhydrous" or "activated for chromatography" and also alumina converted into the anion-exchanger form by treatment with acid), silica gel[34,39,40,44,45,48-57], starch[29,30,32,34,35,48,49,51], Kieselguhr[28,29,34,58,59], glass powder[51-53,60-63], and activated charcoal[47,64-75]. Cellulose[42,49], barium sulphate[29,34,44], gypsum[52], calcium and magnesium carbonates[52,76,77], bentonite[48,78,79], certain metal oxides (zinc[73,75,80-82], magnesium[83,84], lead, lanthanum, and bismuth[82-85], and others), and even ordinary sand[52,53,79,86,87] have also been used.

Application of ion exchangers charged with precipitant ions. This process is interesting because it is thereby possible to remove from solution ions of both charge types at the same time, for example:

$$R^-Ag^+ + NaCl \rightarrow R^-Na^+ + AgCl\downarrow.$$

Gans[88] suggested in 1909 that processes of this kind be used in sorption techniques, referring to an even earlier suggestion by Rümpler[89]. Subsequently this idea was embodied in the so-called silver zeolites, which are widely used for the purification of seawater under special conditions[90]. With the introduction of the synthesis of ion-exchange resins, the application of a cation exchanger in the silver-form was suggested[91] for this purpose, by analogy with the silver zeolite. Somewhat later Gaddis[92] used a weakly basic anion exchanger in the sulphide form instead of gaseous hydrogen sulphides in systematic qualitative analysis. Gaddis's idea was supported and developed further by Kunin[93,94] in 1949, and this was followed by other suggestions concerning the application of ion-exchange resins in the precipitation-chromatographic method: by Aleskovskii and Kheifets[95-98], Glueckauf[99,100], and Kielczewski[101]. Recently ion-exchange resins have been increasingly used in studies on precipitation chromatography (Refs. 102–113 and others).

However, a drawback of such ion-exchange precipitation systems should be noted. This concerns those cases where the solution contains a mixture of ions not all of which form precipitates with the precipitant. In such cases, exchange with the counterions in the solution causes more of precipitant ions to be displaced from the resin than can be consumed in precipitation in the "working" part of the column bed. This can be made clearer by means of an example: suppose that a resin is charged with silver and that the solution contains sodium chloride and nitrate. Sodium displaces from the resin an equivalent amount of silver ions which precipitate chloride ions. Since the ionic concentrations are linked by the relation $[Ag^+]+[Na^+] = [Cl^-] + [NO_3^-]$, it follows that $[Ag^+] > [Cl^-]$. The excess of the unreacted precipitant is washed out of the column with the stream of solvent. Thus the higher is the amount of non-precipitable and non-exchangeable ions (in this example nitrate) the lower is the efficiency of the precipitation-chromatographic column. Ion exchangers are therefore completely ineffective for trapping (precipitating) micro-impurities, for example in the purification of salt solutions. For this purpose, sparingly soluble precipitants are employed.

Sparingly soluble precipitants. In the practical application of precipitation chromatography sparingly soluble precipitants are most frequently used, particularly in paper chromatography. To obtain a precipitate on filter paper, the latter is usually impregnated initially with a solution of one of the reactants, containing as a rule the cation of the precipitate to be formed (since the paper exhibits a higher sorption capacity with respect to cations than with respect to anions). Then the paper is immersed in the solution of the other reactant, whose anion forms the required sparingly soluble compound with the cation present on the paper. It is desirable to wash out the excess of the unreacted salts with pure solvents[20,27,114]. Sometimes the the paper is immediately immersed in a suspension of the previously prepared precipitate[22-27]. Paper is impregnated with sparingly soluble organic precipitants in alcoholic etc. solutions with subsequent drying to remove the solvent[115-118].

Powders of sparingly soluble precipitants are sometimes introduced into the column in a pure form[33,36,76,77,119-125] but most often they are introduced in a mixture with a

filler[28,34-36,60,68]. In most cases the mixture of powders is loaded into the columns in a dry form only ("dry columns"). A homogeneous material can be loaded into columns also in the form of an aqueous suspension (with heterogeneous mixtures there is a risk of layer formation in the preparation of suspensions). An advantage of "wet" columns over "dry" columns is that in the former there are no trapped air bubbles which prevent the operation of part of the charge.

In some cases more than one precipitant is introduced into the chromatographic medium in order to increase the number of absorbing substances[27,48]. On the other hand, certain properties of the chromatographic medium are sometimes improved by using a carrier of more complex composition. For example, Hopf[32] initially impregnated paper with starch and then with the precipitant (violuric acid), probably in order to increase the concentration of the precipitant on the paper. In another study[126] a mixture of finely ground alumina and cellulose pulp, obtained by boiling cotton wool in dilute nitric acid, was used to produce a sorbent with the highest possible surface area and a good filtering capacity. The alumina adhered satisfactorily to the cellulose pulp, the combined carriers being subsequently charged with the precipitant (phosphate).

The carrier (filler) can also take a more active part in the precipitation absorption process. Thus, according to Napol'skii[87,127], the addition of magnesium or calcium oxide to dimethylglyoxime helped maintain in the column the optimum acidity of the medium for the precipitation of nickel (pH $\geqslant$ 6):

$$\begin{cases} NiSO_4 + 2\,H_2Dm \rightleftarrows Ni(HDm)_2\downarrow + H_2SO_4\,, \\ H_2SO_4 + MgO \rightarrow MgSO_4 + H_2O\,. \end{cases}$$

In some cases columns consisting of several beds with different precipitants were used[30,87,97,128-131] to ensure selectivity of absorption and a clear-cut separation of a number of substances[132].

It is noteworthy that a fairly widely used method of preparation of the precipitation-chromatographic medium, in which a readily soluble precipitant is introduced into the carrier, is erroneous. For example, columns with mechanical mixtures of a carrier and a readily soluble precipitant are used fairly frequently, the fraction of the precipitant amounting sometimes to 10–50% of the charge[39,40,44,48,108,133-137], or paper is impregnated with a solution of a readily soluble salt and then dried without washing[138-145]. In experiments with the usual carriers having low sorption capacity (paper, alumina, etc.) such a technique is undesirable, since soon after the start of filtration of the solution the excess of the precipitant, not fixed on the carrier by sorption forces, is washed out of the latter. Only in rapid processes (for example in spot reactions) can the substance react more or less completely with the precipitant. On the other hand, under the usual conditions of the chromatographic process, such technique is ineffective. It is even less applicable in quantitative analysis based on the size of the precipitation bands, which requires uniform distribution of the precipitant in the chromatographic medium (see below). The advantages of sparingly soluble precipitants in systems resembling those used in precipitation chromatography were pointed out by Clarke[146,147] as early as 1937. Investigators who used the precipitation-chromatographic method for quantitative analysis arrived at the same conclusion[62,114].

Among other principles of carrier and precipitant selection, one may note the tendency (in those cases where it is possible) to choose white or pale coloured carriers and precipitants, which form coloured precipitates with the ions evolved. In most real cases this can be fairly readily achieved and the investigator then secures the valuable advantage of being able to follow the process during the separation period and to correct the operation as required. To make observations on precipitates whose colour does not differ from that of the background, a phosphor may be introduced into the column before the experiment[48].

IV. PRECIPITATION-CHROMATOGRAPHIC METHODS OF SEPARATION

A fairly wide variety of procedures for the separation, purification, and concentration of substances is already used in precipitation chromatography. However, the possibilities of precipitation chromatography are still far from being exhausted and eventually the number of methods should probably increase considerably. The present situation in this field must be regarded as merely the initial stage of development.

One of the simplest chromatographic procedures based on precipitation chromatography consists in selective absorption of one of several substances in a solution passed through a suitably prepared column or impregnated paper. This method is widely used both in the concentration of substances from dilute solutions[62,87,146-148] and for the removal from solutions of specific interfering impurities[64-68,71-75,80,104,105,149,150]. In both cases precipitation chromatography has significant advantages over other methods used for the same purposes. In the first case (concentration) the minimum concentration at which a given substance can be absorbed from solution is usually very low as a result of the very low solubility products of the precipitates formed. This permits virtually quantitative isolation from solutions of components present even at microconcentrations[103,151]. On the other hand, ion-exchange resins and the usual sorbents are not very suitable for the removal of microimpurities from salt solutions at high concentrations because of insufficient differences in sorbabilities[73], while precipitation systems readily overcome this difficulty.

The advantages of precipitation under chromatographic conditions compared with static conditions are evident: the technique is simpler, the number of operations required is smaller, the time needed is shorter, the efficiency of separation is higher, and the risk of losses and contamination during the separation process is lower. We may quote the following examples of the significant simplification of technique. It has been suggested that in partition paper chromatography of alkali and alkaline earth metals the interference of polyvalent ions be eliminated as follows[152]. Polyvalent anions are precipitated from the solution as sparingly soluble lead salts at the beginning of the chromatographic band (not far from the start), where two drops of lead acetate solution are deposited before the start of the experiment; at the same time the test cations pass freely through the lead spot and move further along the paper in the usual order. Precipitation in chromatographic columns and not under static conditions is particularly desirable in those by no means rare cases[153,154] where colloidal precipitates are formed, since precipitation-chromatographic media quite often show a satisfactory capacity for the retention of colloids.

Many studies have been described in the literature on the separation of two and more substances by the selective absorption of some and the free passage of other mixture components[47,101,112,155,156]; in this way it is possible to separate ions and substances with similar properties[44,47,54,59,76,77,87,127,157-161].

Adequate selectivity of absorption under real conditions can be ensured both by the selection of the appropriate precipitant and, in the case of ion-exchange carriers, by the choice of an ion exchanger with the required acidity or basicity [92,99,100]. For this purpose (to ensure the specificity of absorption), Hesford [47] suggested that activated charcoal be saturated with bases differing in their dissociation constants: aqueous ammonia, methylamine, diethylamine, urea, ethanolamines, alkylamines, hexamines, pyridine, and others. Strong bases were used to separate most of the cations, forming insoluble hydroxides, from alkali and alkaline earth metals, while weak or complex-forming bases were used for the isolation or separation of particular cations.

Substances retained in the columns are then eluted with solutions of acids, alkalies, or complex-forming agents. Another separation procedure is based on the choice of a selective solvent, which elutes only one or some of the components to be separated which are retained in the column [47,63,111]. For example, on the alumina and cellulose pulp columns [126] mentioned above, silver and iron(III) ions were absorbed in the form of the phosphates and then eluted successively with 0.1 *N* acetic acid (silver) and hot 2 *N* hydrochloric acid (iron). The separation was quantitative. Kielczewski used an unusual procedure [110] for the separation of silver and copper(II) on an anion-exchange resin saturated with arsenate. After both silver and copper had been absorbed on the resin, hydrochloric acid was passed through the column. This resulted in the elution of copper, while the silver arsenate precipitate was converted into silver chloride, so that silver remained in the column. Subsequently silver was eluted with aqueous ammonia (complex-forming solvent).

Precipitation-chromatographic methods on paper differ little from the usual paper chromatographic procedures. Both linear and circular chromatograms are produced. A definite volume of the test solution is usually deposited with a capillary on impregnated paper and the chromatogram is then eluted with a pure solvent until the stabilisation of the zone boundaries. Sometimes dilute solutions can be applied to the paper continuously, i.e. by simple impregnation of the paper with solution at one end [162,163]. The thin-layer precipitation chromatographic technique [55-57] is in many ways similar to paper chromatography.

When a clear-cut detection of all the zones is required on paper or in a column, the primary chromatogram obtained (as a result of the passage of the initial solution) is washed with water or weak aqueous solutions of mineral salts; sometimes it is washed also with organic solvents [54,118,164-166]. If necessary the zones can be revealed by means of solutions or vapours of the usual reagents [22-24,109,139-145,167], or, especially in columns, by means of adsorption indicators introduced with the test solution [137,168-171].

When the primary precipitation chromatogram is washed with organic solvents, the components of the mixture on impregnated paper are frequently separated by elution [115-117, 172,173]. Possibly, it is more correct to regard these as cases of partition rather than precipitation chromatography.

One of the varieties of precipitation chromatography is a separation procedure in which absorption in the solid phase is due to an oxidation–reduction reaction with formation of a sparingly soluble reaction product [8,109]. An example of the application of this method is the use of manganese zeolites [174] for the removal of iron(II) and manganese(II) from water (in cases where the possibility of the preliminary aeration of water is limited and in certain others). The manganese zeolite is a source of oxygen which oxidises the divalent iron and manganese ions to the trivalent state, this being accompanied by the precipitation of the hydroxides. Oxidant additives (sodium permanganate) were used earlier in [175] gas mask filters. A small amount of the oxidant in the gas mask (about 3%) served to oxidise certain gases, for example arsine, which are poorly sorbed by activated charcoal and soda lime (the principal components of the gas mask filter). It has recently been suggested [176] that precipiation-chromatographic columns with a silver precipitant be used to trap arsine (from the gas phase):

$$AsH_3 + Ag^+ \rightarrow Ag_3As\downarrow + Ag^0 + AsO_3^{3-}.$$

The reducing properties of certain ion exchangers, including electron-exchange resins, have found application in the extraction (concentration) of noble metals from solutions [106,107,177].

We may mention yet another method—the procedure for the preparation of stable sols with the aid of precipitation-chromatographic columns [43,44,94,178,179]. In general this method cannot be regarded entirely as precipitation chromatography, since for this purpose one selects a special carrier, which, while retaining the precipitant, should not retain in the column the resulting colloidal precipitate. For example, the following processes have been achieved on ion exchangers [179]:

$$R(OH)_3 + AlCl_3 \rightarrow RCl_3 + Al(OH)_3\downarrow,$$
$$R'H_2 + Na_2SiO_3 \rightarrow R'Na_2 + H_2SiO_3\downarrow.$$

The sols obtained are very pure.

Yet another application of precipitation chromatography is the procedure for the quantitative determination of organic acids on paper impregnated with a hydroxide [180,181]. The quantitative analysis is based on the measurement of the area (or weight) of the section of the paper freed from the hydroxide precipitate as a result of dissolution by the test acid.

V. DIFFUSIONAL PRECIPITATION CHROMATOGRAPHY

The difference between the unusual variety of precipitation chromatography and the normal procedure is that here the principal mass-transfer mechanism is diffusion and not filtration of the solution. The specificity of the reaction medium consists in the fact that the latter does not permit the filtration of the solution and convective mixing of the substances. Such media include moisture-saturated porous materials [44,130,182,183], solutions in capillaries [184-186], and gels. The last are used most often, and therefore such chromatograms are also called "precipitation chromatograms in gels" [185-188]. The brief, accurate, and general name given in the heading of this section was proposed by Olenovich et al. [189].

The technique of this method is very simple. A fused gel of gelatin, agar-agar, or a similar substance, to which the precipitant had been introduced earlier in the form of a solution, is poured into test tubes or Petri dishes. When the gel has set, the test solution is poured onto its surface (in Petri dishes in the form of individual drops). The diffusion of the components of the solution into the gel is accompanied by the precipitation of the various deposits, which results in the continuous development of the chromatogram [185-196].

Some investigators have used paper impregnated with gel together with the precipitant [197,198]. Diffusional precipitation chromatograms can also be obtained in capillary tubes sealed at one end and filled with a precipitant solution (without gel) [185,186,199]. Such capillaries are simply immersed in the test solution with their open ends downwards.

A modified technique is used for special purposes: counter-diffusion of reacting substances in a pure gel medium [182,183,200-202].

VI. THEORY OF PRECIPITATION CHROMATOGRAPHY

1. Problems of Precipitation Sorption

The term "precipitation sorption" includes any processes where the absorption of a substance in an already existing solid phase involves the formation of a new solid phase due to the production of a sparingly soluble compound by a chemical reaction. This precipitation sorption is a complex process. In one of its stages the solute reacts with the precipitant which leads to the precipitation of a sparingly soluble compound. The following, no less important stage is the fixation of the newly formed precipitant in the solid phase. The nature of this fixation can be extremely varied—ranging from mechanical retention to adhesion or molecular fixation. The successful absorption of a substance in a precipitation-chromatographic system depends not only on the correct choice of the precipitant but also on the choice of the carrier which is capable of firm retention of the precipitates formed.

The present author [203] derived an equation for the isotherm of ionic precipitation absorption taking into account only the solubility of the precipitate (i.e. assuming that the precipitate is completely and firmly retained in the solid phase). It was found that the isotherm exhibits virtually maximum convexity. According to the familiar postulates of chromatographic theory, a number of important conclusions follow from this finding. When the isotherm is convex, dynamic precipitation sorption takes place with the formation of the so-called steady-state front, i.e. under conditions of parallel transfer of the sorption front. In those cases where the influence of the sorption kinetics or various longitudinal flow perturbations is weak, the effect of the convexity of the isotherm (tending to sharpen the front of the sorption wave) is particularly pronounced. As a result, exceptionally distinct zone boundaries are particularly frequently observed in precipitation chromatography [8,39,44].

Precipitation sorption on sparingly soluble precipitants. Earlier it was noted that in the practical application of precipitation chromatography, substances which are sparingly soluble in the solvents used but can react with the ions subjected to chromatography, forming even less soluble products, are employed very often as precipitants (the present author suggests that such precipitants be referred to as sparingly soluble). For example, zinc sulphide can absorb copper, cadmium, silver, and other ions, since the sulphides of these metals are even less soluble in water than zinc sulphide. The inclusion of such heterogeneous displacement reactions in precipitation-sorption processes is consistent with the generally accepted definition of a bulk-phase chemisorption reaction: "the absorption process due to a heterogeneous chemical reaction gradually spreads throughout the bulk of the solid, ... producing a new substance in the form of a new phase" (Lepin' [204]).

The absorption of ions on sparingly soluble precipitants is sometimes difficult to distinguish formally from ion exchange. Hayek [9] suggested that two varieties of formal ion exchange be distinguished: ion exchange on relatively high-molecular weight substances without appreciable change of structure, for example:

$$Ca_5(PO_4)_3OH + F^- \rightleftarrows Ca_5(PO_4)_3F + OH^- ,$$

and with change of structure of the initial substance, for example:

$$AgCl + Br^- \rightarrow AgBr + Cl^- .$$

The present author believes that the inclusion only of reactions of the second kind (with change of structure, i.e. with formation of a new solid phase) among precipitation processes is quite acceptable. For example, on the basis of the same considerations, one is quite justified in including among precipitation chemisorbents also the large class of sparingly soluble complex-forming precipitants (of the type of dimethylglyoxime and hydroxyquinoline), despite the apparent complexity of their molecules.

Precipitation sorption on ion exchangers. The application of ion exchangers in precipitation chromatography is based on a three-stage process [8,205,206]: (1) displacement of the precipitant ion from the resin by ion exchange; (2) its reaction with the ion undergoing chromatography leading to the formation of sparingly soluble compounds; (3) fixation of the precipitate on the resin. It has been established [205,206] that on synthetic resins with a high exchange capacity, the ion exchange and formation of a sparingly soluble compound can be clearly distinguished both in time and in space. The ion-exchange displacement of the precipitant ion A linked to the resin matrix R:

$$R^-A^+ + B^- + M^+ \rightleftarrows (R^-M^+ + A^+) + B^- ,$$

results in the binding of the ion B in the precipitate,

$$A^+ + B^- \rightarrow AB\downarrow$$

only after the liberated ions A have diffused to the surface of the resin grain. The explanation is that, as a result of the Donnan potential, the free electrolyte BM virtually does not enter the resin phase [94,207]. Helfferich [208], who considered the problem of the kinetics of ion-exchange processes accompanied by any chemical reaction, recently arrived at similar conclusions. Thus the view that the precipitates are formed and fixed within resin grains [103,105,110] must be regarded as erroneous.

The problems of the equilibrium in the system ion exchanger—sparingly soluble electrolyte—water have been examined in a number of studies [207,210-215]. Grigorov and Tarshis [209] demonstrated the equivalence and the reversibility of ion exchange accompanied by a chemical precipitation reaction. To show this, three successive ion-exchange cycles, including the reaction of barium chloride (or potassium sulphate) solution with the ion exchanger in the silver (or barium) form and the regeneration of the resin with a solution of silver nitrate (or barium chloride), were carried out. Despite the increasing amount of the precipitate (silver chloride or barium sulphate), the amounts of the ions undergoing exchange remained virtually constant in all three cycles. In general the possibility of the regeneration of the column without eluting the absorbed substance [106,107,113] is one of the valuable features of precipitation chromatography. For example, after a number of repetitions of the absorption–regeneration cycles on an electron-exchange resin, it is possible to accumulate reduced silver in amounts up to 300–400% of the weight of the resin [107].

Koblyanskii and Kameneva [216] observed higher rates of ion exchange in a cation-exchange column if the exchange was accompanied by the formation of a precipitate; this is

explained by the displacement of the ion-exchange equilibrium to the right. On the other hand, the general form of the elution curves revealed a dependence both on the solubility product of the precipitate formed and on the constant for the exchange of the corresponding pair of ions. The present author [205,217] showed that conditions of parallel transfer are established in the motion of the precipitation-sorption wave in cation-exchange and anion-exchange columns regardless of the constants for the exchange of the corresponding ions. He also developed a mathematical theory of dynamic precipitation sorption on ion exchangers.

Elsewhere [205,206] he discussed the problem of the mechanism of the fixation of the precipitate on the surface of the resin grains. The following probable mechanism of the fixation by adhesion of the peptised precipitate AB on the resin R was proposed:

$$R^-A^+ + B^- + M^+ \rightarrow R^-M^+ \cdot (B_n^- \cdot AB) + nM^+ ,$$

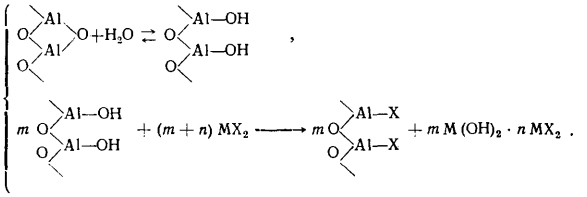
where part of the ions M remain in the diffusion layer at the precipitate particles.

Precipitation sorption on alumina and certain other inorganic sorbents. Because of its wide use in the chromatography of inorganic ions, alumina has attracted the attention of many investigators who attempted to elucidate the sorption mechanism. Gapon [38,218,219] believed that the absorption of cations on basic alumina and the absorption of anions on acid (treated with acid) alumina is due to ion exchange at the aluminate group:

$$(Al_2O_3)_mAlO_2 \cdot Na + A^+ + B^- \rightleftarrows (Al_2O_3)_mAlO_2 \cdot A + Na^+ + B^- ,$$
$$(Al_2O_3)_mAlO \cdot NO_3 + A^+ + B^- \rightleftarrows (Al_2O_3)_mAlO \cdot B + A^+ + NO_3^- .$$

The sorption of polyvalent anions on basic alumina and polyvalent cations on acid alumina was explained in the same papers [218,219] by the reversal of the charge on the sorbent surface by the polyvalent ions.

Without rejecting the possibility of the absorption of ions by ion exchange on alumina, most investigators nowadays believe that a hydrolytic absorption mechanism [9,17-19,84,85,220,221] is more likely for heavy metal salts on basic alumina, for example [81]:



Heavy metals are sorbed as precipitates of hydroxides or basic salts, for example $Cu_2(OH)_3Cl$ from $CuCl_2$ solutions [83,84,222,223], $Co_2(OH)_3Cl$ from $CoCl_2$ solutions [84], and $Cu_4(OH)_6SO_4$ from $CuSO_4$ solutions [84].

The capacity for hydration, which determines the absorption capacity of alumina, depends on the heat-treatment of the latter in its preparation from the hydroxide [223-225]. This capacity is a maximum for γ-alumina (the cubic form) obtained by heat treatment at about 600°C and is absent in the α-form (the rhombohedral form) formed on heating above 1200°C.

It has been noted [84,85] that the same hydrolytic mechanism accounts for the absorption of heavy metals on certain other basic substances, for example on magnesium or lanthanum oxides (as well as on anion exchangers in the hydroxide-form). The absorption of strong electrolytes from aqueous solutions on charcoals is regarded as hydrolytic [175,226-228]. This is indicated by the similarity (with certain unimportant exceptions) of the sorption series for heavy metals on basic alumina [15,16,19,85,133,221,229,230], lanthanum oxide [85], partially dehydrated ferric hydroxide [125], and on charcoal [231], both to one another and to the series of the solubility products of the hydroxides of these metals [232].

The sorption of heavy metals on alkaline silica gel is attributed to the formation of sparingly soluble polysilicates [233]. Here the polysilicate macroion of silica gel serves as a precipitant ion for certain metals. The same sorption series was obtained as for the solubilities of the silicates [233,234].

Certain anions are also sorbed on alumina by a precipitation mechanism [82]. In those cases where alumina is used as a carrier with a sorbed precipitant it is not always possible to observe the fixation of the newly formed precipitates on the carrier [39,43,44]. If the precipitate was nevertheless retained in the column, it was found [205,206] that the individual crystals of the precipitate are fixed on the surface of the grains of alumina (both basic and acid). Since the nature of these adhesion forces is not entirely clear, it is so far necessary to choose empirically the conditions under which the precipitation-chromatographic process can be successfully taken to completion (without loss of the precipitates).

2. Conditions for the Formation of Precipitation Chromatograms

The main factor which determines the separation of substances in precipitation chromatography is the difference between the solubilities of the precipitates formed [39]. Being a variety of the chromatographic method, precipitation chromatography is a dynamic process with multiple repetition of the fundamental step [8,53]. Schematically the formation of precipitation chromatograms can be described as follows [235]. When fresh portions of solutions enter a given element of the column (or impregnated paper), the component which reacts with the precipitant to yield the least soluble precipitate displaces the appropriate components from the previously formed more soluble precipitates. The displaced components move further with the solvent stream and are again precipitated in those layers of the column where there is either the free precipitant or a more soluble precipitate with other components. Frequent repetition of such redistribution of material in the direction of the stream leads to the formation of a developed precipitation chromatogram.

Two evident conditions must be satisfied for the formation of a precipitation chromatogram. In the first place the precipitate must be fixed in some way in the solid phase of the chromatographic medium and should not be eluted with the solvent stream [54,78,109,236] and in the second place the precipitates formed must be retained at the site of their precipitation [8,40,53,147,236-238].

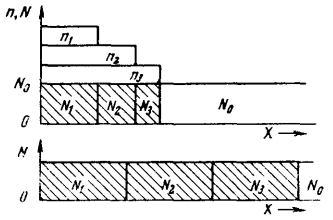
3. Structure of Precipitation Chromatograms

The sequence of the zones in precipitation chromatograms depends on the order of precipitation of the corresponding substances [8]. In the determination of the sequence of the zones one examines in the first place the relative solubility products of the precipitates and in addition the relative concentrations in the initial solution of the substances being separated [8,239]. The present author has given a rigorous mathematical derivation of the general

relations whereby the sequence of the zones in precipitation chromatograms can be predicted[240].

Gapon[43,44] proposed an approximate method for the determination of the zone sequence from reduced solubility products. Although this method is not quite rigorous (for this reason certain exceptions to the rule are observed)[44], in the majority of cases it gives a qualitatively correct picture. In Gapon's method the solubility products of the precipitates are compared after being raised to a power equal to the smallest common multiple of the number of precipitant ions in the precipitate molecule [the factor by which the number of precipitant ions in the precipitate molecule has to be multiplied to give the smallest integral common product (Ed. of Translation)]. For example, in the comparison of the solubilities of iron(III), copper(II), and silver(I) their solubility products are raised to the second, third, and sixth power respectively. The zone sequence (beginning at the start) should correspond to the sequence of increasing values of the quantities thus obtained.

In contrast to the other varieties of chromatography (molecular, ion-exchange), for precipitation chromatography with considerable differences between the solubilities of the resulting precipitates, theory predicts[205,239,241] a simple structure of the chromatogram with virtually only one component of the initial mixture (see Figure) in the solid phase of each zone. In the primary chromatogram some zones, in particular the first (at the start), may still contain admixtures of other components of the initial mixture in the form of a free solution, but in the washed chromatogram every zone contains only one component each. The zones follow one after another without discontinuities, usually with very distinct zone boundaries.



In the ideal case the ratios of the concentrations of the precipitant in the carrier (N_0) and the densities of precipitation (N_1, N_2, N_3, ...) should be equivalent. Under real conditions this requirement is satisfactorily met on finely dispersed sorbent-carriers[52,53,62,205,236].

The washing of the primary chromatogram with an indifferent solvent leads to the widening of the primary zones (particularly those further removed from the start), but only up to a certain limit, beyond which further washing virtually does not change the chromatogram[238,242]. This limit is determined by the amount of substance introduced and the precipitating capacity of the medium[235].

The distribution of the precipitates in the washed chromatogram has been little investigated by direct analysis. In some cases[78] insufficiently complete separation was observed in zones close to the start, although the zones were clearly distinguished by colour. The present author investigated[205,241] the reasons for the incomplete separation in certain specific systems. It was established that in highly dispersed inorganic ion exchangers charged with a precipitant ion, the contamination of initial zones by other components of the initial mixture can be accounted for by the adsorption coprecipitation of ions on the precipitates of the main substance; this occurs to a small extent. On sparingly soluble precipitants and in particular on ion-exchange resins charged with precipitants there is also a poor separation of mixtures in the chromatographic medium due to kinetic causes (continuing precipitation of impurity components from the free solution after formation of the primary chromatogram, when there is not sufficient time for the complete consumption of the precipitant during the brief period when the primary chromatogram is formed). To improve the separation in this last case, it is recommended that the primary chromatograms be washed immediately when the filtration of the initial solution is completed.

4. Quantitative Analysis by Precipitation Chromatography

In view of the very great simplicity of precipitation chromatograms (see Figure), simple quantitative determination of the components from the size of their zones in the chromatograms is possible. One of the conditions for quantitative analysis by precipitation chromatography, together with those enumerated above (see Section VI, Subsection 2), is the uniformity of distribution of the precipitant in the chromatographic medium[8,62,205,236,238].

Washed chromatograms. When washed chromatograms, which virtually do not contain the substances being analysed in a free form (see Figure), are used, a simple linear relation between the quantity of the component introduced and the size of its zone is obtained. The size of the zone is defined as follows: in column chromatography the volume or height of the zone[34,35,50,123,243], in paper or thin-layer linear chromatography the length[21,24-26,55,57,162,244-256], the area[166,257-273], or the weight of the zone[274-277] after the latter has been cut out, and in circular chromatography the area of the circular and annular zones[114,278,279].

Quantitative analysis by precipitation chromatography has proved so simple and convenient that in certain cases it has been used as a simple final step in analytical determinations. For example, it has been suggested[255,262] that partition and precipitation chromatography be combined, the first method being used to separate the ions and the second for their quantitative analysis, after the individual components have been transferred with the aid of appropriate solvents from the chromatograms where they had been separated to paper impregnated with the precipitants.

Although usually quantitative analysis by precipitation chromatography is used for the analysis of a single precipitable substance, there have also been studies on the quantitative determination of components in complex chromatograms[34,35,123,244,248,251,254,258,272,273]. The present author's investigation in this field[205,241] showed that, despite the partial retention of certain mixture components in zones other than their intrinsic zones (see above), the relations between the sizes of washed zones in complex chromatograms and the concentrations of the corresponding components in the initial solutions (for a constant sample volume)

remain linear or nearly so. As a result, quantitative analysis of complex mixtures by frontal precipitation chromatography is possible without preliminary separation.

In the chromatography of various ions on media with sparingly soluble precipitants a steady increase in the length (or area) of the zones with increasing solubility products of the precipitates was observed[62,78,114]. Kulaev[141,143,144] relates the velocity of the precipitation front directly to the solubility product, which of course is unjustified. The present author believes[205,241] that the above relation is due to differences in the rates of the reactions of the solution components with the precipitant. The rate of the displacement reaction is higher the greater is the difference between the solubility products of the starting material and the final product.

Primary chromatograms. Some investigators have used primary unwashed chromatograms for the quantitative analysis of a single precipitable component[51,78,135,137,168,170,280-285]. The zone size–concentration calibration graphs are then curves concave towards the zone size axis. The reason for the non-linearity of the calibration graphs is that part of the solution does not react with the precipitant, since it is retained by capillary forces behind the precipitation front in the free volume of the column[205,236]. Thus Stefkin[286] obtained a linear calibration graph over a fairly wide range of concentrations (0.016–0.5 M) even though he used unwashed chromatograms, but the latter were obtained by filtration at a reduced pressure: the solution was then drawn downwards in its entirety, without begin retained in the free volume of the column.

An equation for the relation between the size of the precipitate zone and the concentration of the initial solution and certain other factors was derived by Cetini and Ricca[238] and more rigorously by the present author[205,236]. The present author used this equation[205,236] as a basis for a more accurate and simpler method of quantitative determination of a single precipitable substance from the primary precipitation zone using linear calibration graphs in transformed coordinates (the reciprocal of zone size plotted against the reciprocal of concentration).

The present author[205] has also proposed a method of quantitative determination of a single precipitable substance from a primary circular zone, in which a very simple technique is employed. To determine the concentration of the solution, it is necessary to immerse a "wick" of impregnated paper into the test solution and then terminate the impregnation with solution at any convenient time: after drying the paper, it is necessary to measure the ratio of the radii of the solvent front and the precipitation zone (or the ratio of the areas of the corresponding circles). Mathematical analysis showed that linear calibration graphs are obtained when the square of the ratio of the radii or [the ratio of (Ed. of Translation)] the areas of the circles are plotted against the reciprocal of concentration. However, it should be noted that the use of primary chromatograms for quantitative analysis becomes ineffective at relatively high concentrations, and therefore in the general case it is more desirable to employ washed chromatograms.

The maximum dilution method. This method, proposed by Shemyakin and coworkers[5] is used in some cases for the quantitative determination of single precipitable substances[109,111,141,144,169,287-292]. The method consists in a number of successive dilutions of the test solution until the latter gives a negative qualitative response with respect to the ion being determined when tested on a precipitation-chromatographic medium. In preliminary experiments it is necessary to determine the minimum detectable amount and also an empirical "correction for losses", which is about 3–10%.[8] The method has very little accuracy[141], is laborious (particularly in the column version), and is suitable only for approximate determinations of microconcentrations[292].

5. Secondary Phenomena

The various processes involving changes in precipitation chromatograms after formation are combined under the common name "secondary phenomena in precipitation chromatography"[8,41-44,183,293-296]. In laboratory practice secondary phenomena are encountered very rarely (only in special cases) when washed chromatograms are obtained. However, in unwashed (primary) chromatograms, where the chromatographic layer contains free solutions at fairly high concentrations in addition to the precipitate, there is an extremely wide variety of secondary phenomena. In contrast to the requirements of analytical practice, where usually only washed chromatograms are dealt with, the study of secondary phenomena in precipitation-chromatographic processes under natural conditions (for example, in the investigation of certain ore-formation and soil-formation processes) is of exceptional importance.

The major proportion of secondary phenomena in precipitation chromatography consist in the effects of diffusion processes[294,295], which are frequently accompanied by various chemical reactions. In the precipitation chromatograms of the iodides of mercury, bismuth, and lead secondary complex-formation reactions combined with diffusion processes have been noted[43,44,295].

Very frequently (and both in washed and unwashed chromatograms) recrystallisation of the precipitates is observed, leading to the growth of bigger crystals at the expense of a large amount of small crystals[44,205,206]. The recrystallisation of precipitates is a favourable process from the standpoint of the firm fixation of the precipitate in the chromatographic media. Both the solubility and the extent to which the precipitates are dislodged are greatly reduced. However, the subsequent elution of the absorbed substance from the column becomes more difficult.

The disruptive effect of precipitates in porous media noted in some cases deserves attention[41,297].

6. Theory of Diffusional Precipitation Chromatography

In diffusional-precipitation systems the velocity of the precipitation front depends on a number of factors: the ratio of the diffusional capacities of the outer and inner electrolytes[298], the concentrations of the outer electrolyte[185,186,190,205,299,300], the inner electrolyte (precipitant)[205,300], and the gel[185], and also the solubility of the precipitate formed[198]. The relative contributions of all these factors in fact determine the form of the diffusional-precipitation chromatogram.

It has been shown[205,298,300] that analytical solutions available from the theory of diffusion[301] and thermal conductivity[302] cannot be applied directly to diffusional-precipitation systems. At the same time an adequate mathematical description of diffusion complicated by precipitation is so far lacking.

The simplest theoretical examination of precipitation diffusion, postulating a linear process[205,303], leads to the

conclusion that the ratio of the square of the depth of the precipitation zone to the time elapsed is constant if the concentration of the outer electrolyte remains constant. The validity of this hypothesis has been firmly established by numerous experimental investigations [303,304].

Diffusional precipitation with a non-constant source was investigated by Watanabe [305] and Mofávek [306]. The equations obtained by Mofavek describe the process more accurately [205,300].

Krishnamurti and Dhareshwar [198] observed empirically a relation between the height of the precipitation zone x and the solubility of the precipitate S. Using the diffusional precipitation (in an agar gel) of silver salts with ten anions of different valence types as an example, the relation was found to be of the form

$$x = k + k' \lg S \ ,$$

where k and k' are constants characterising a number of precipitation systems with a common precipitant ion.

In his study of the rate of penetration into the gel of the precipitation front for different (constant in time) concentrations of the outer solution c_0 the present author observed the following relation [205,300]:

$$x = (a + b \lg c_0) \sqrt{t} \ ,$$

where a and b are constants which depend on the concentration of the precipitant in the gel and t is the time. Using this equation, it is possible to improve the accuracy of, and make more convenient the quantitative analysis of solutions by the diffusional-precipitation method [196,299], which is simple and not at all laborious [205,300].

It has been noted [185] that the change in the density of the gel has little effect on the velocity of the precipitation front. Probably the Traube–Shikata rule [307], first established for the diffusion of dyes in gels, namely $\sqrt[3]{c_g D} =$ const. (c_g is the concentration of the gel and D the diffusion coefficient), holds in diffusional-precipitation systems.

Since a washed chromatogram cannot be obtained in diffusional-precipitation systems, one cannot expect the separation of the mixture components into individual zones: the liquid phase of the gel will contain all other initial-solution components, which form with the precipitant more soluble reaction products. Here we have the same situation as in the usual primary chromatograms: the visual separation of the chromatogram into zones (according to the colour of the precipitates) is not by itself evidence of sufficiently complete separation of the mixture.

The distribution of concentrations in diffusional-precipitation chromatograms is much more complex than in the usual chromatograms. The distribution along the column of precipitate of even a single substance is fairly complex, the chromatogram including bands of different colour and degree of transparency (depending on the size and amount of the precipitate crystals [308]). The zones of adjacent precipitates are sometimes separated by a region of the gel free from precipitate [185-187,192,195]. The effect of the precipitant concentration and the concentrations in the outer solutions, and the gel on the size of this region was investigated by Milone et al. [192].

Various repetitive structures, the so-called Liesegang rings [309,310], are fairly frequently superimposed onto the general pattern. However, it has been shown [205,298,311,312] that the presence or form of such structures in no way affect the principal features of the motion of the diffusional-precipitation zone front.

VII. APPLICATIONS OF THE METHOD

Examples of various applications of precipitation chromatography have already been noted above. Certain common precipitates for the separation of inorganic ions are indicated in the bibliography [327-355].

Among the traditional ways of using the precipitation-chromatographic method, one of the most important is qualitative chemical analysis [13,14,92,102,117,133,136,142,146,147,195,313,314]. A classical example of sensitivity and specificity is the qualitative test for nickel, which is carried out on a dimethylglyoxime column: the minimum detectable amount is 0.2 μg in the presence of a ten thousand-fold excess of cobalt [76,77].

Quantitative analysis by precipitation chromatography is used mainly for inorganic ions. The method has been employed for the analysis of metals and alloys [34,35,86,119,120,140,245,246,249,250,271], minerals [119,120,196], natural waters [163], various biological materials [86,152], and food products and materials used in the food industry [109,134,168,169,287-290,315]. Apart from inorganic ions, the substances separated and analysed have included organic acids [165], lower aliphatic amines [54], phenols [267,273], reducing sugars [261], and various pharmaceutical preparations [48,187,188,316].

Precipitation chromatography has found wide application in the thorough purification of salt solutions (removal of microimpurities), for example in the purification of salts for the preparation of phosphors [64-66,68,72,73,80,104,105,149,150,317-319]. The residual content of heavy metals in the products does not exceed 10^{-5}–10^{-6}%. The methods proposed are very economical, simple, and convenient. For example, it is possible to purify hundreds of kilograms of zinc or cadmium sulphates, giving "chemically pure" materials, by simple filtration through 1 kg of sorbent containing about 48 g of dimethylglyoxime [75].

James and Welch [103] used successfully anion-exchange resin columns charged with precipitant ions for trapping fragment elements from solutions without carriers, and they have noted that the method is superior to the usual coprecipitation procedure as regards efficiency and selectivity. Golovatyi and coworkers [62] demonstrated the possibility of the quantitative concentration of inorganic ions from solutions diluted by a factor of 75–100 relative to the minimum detectable amount (as shown by the colour reaction). The principles of precipitation chromatography have been used for a long time in the purification of water [90,91,174].

Precipitation and diffusional-precipitation chromatography are used to elucidate and model ore-formation processes [182,183,190,297,320-326].

After this article had been submitted to the editors, new papers have been published on precipitation chromatography in the column version [356-363], in particular in ion-exchange resin columns [364-371], and also on paper precipitation chromatography [372-391]. The above publications include also certain earlier papers, which the present author missed previously.

As before, the greatest number of publications deal with the quantitative analysis of inorganic ions on impregnated paper [373-384,389-391]. Small amounts of substances can be detected with the aid of columns [358,361,364]. Precipitation chromatography is used for quantitative inorganic analysis [388], purification of salts [356], quantitative separation of inorganic ions [366-368,386], and radiochemical separation on ion-exchange resins [369-371], including the separation of genetic isotope pairs (for example, $^{90}Sr + {}^{90}Y$, $^{140}Ba + {}^{140}La$). Some papers also deal with the problem of the theory of precipitation sorption [359,360,362,363,365].

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Structure Formation in Disperse Systems in an Electric Field

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The application of an electric field to disperse systems usually results in the aggregation of the particles of the dispersed phase and their organisation into characteristic structures oriented along the lines of force. Processes of this kind are observed both in finely dispersed colloidal systems and in coarsely dispersed systems–emulsions, suspensions, powders. Despite the extremely varied phenomenological picture of the structure-formation processes, which in many respects is due to the nature of disperse systems, the mechanisms and dynamics of their development also have much in common. Analysis of the fundamental mechanism and the kinetics of these processes constitute the theoretical aspect of the problem of structure formation in disperse systems in an electric field.

Apart from the purely theoretical interest, the problem does not lack practical importance. It is sufficient to say that structure-formation processes underlie phenomena such as, for example, the breakdown of liquid dielectrics and the dehydration of petroleum in an electric field.

In this review an attempt is made to give a brief outline of the historical development of the problem, to characterise its present state, and to suggest the possible ways in which it may develop further. As far as we are aware, the structure-forming effect of an electric field on disperse systems was first described by Rafinesque[1] and Hohlfeld[2], who observed the formation on the surface of a charged object of thread-like structures made up of smoke particles.

The investigations of Munk af Rosenschöld[3,4], who must be regarded as the original discoverer of the coherer and who anticipated Branly by half a century, were carried out in the 1830's. In his experiments a tube filled with wood charcoal powder in an electric circuit completed the circuit under the influence of electric discharges occurring in its vicinity; when the tube was shaken, the circuit was reopened. In the 1880's studies on the electrical conductivity of metallic powders were renewed and led to the discovery of coherers or fritter-detectors of electromagnetic

waves. The work of Calzecchi-Onesti[5] and Branly[6,7] must be mentioned as foremost among the investigations in this field. Branly's coherer consisted of a glass tube filled with metal filings and incorporated into the circuit. Since at that time coherers were the only detectors of electromagnetic waves available, they were thoroughly investigated. Towards the middle of the 1890's it became evident that, firstly, the coherer effect arises only when the conducting material is dispersed in a dielectric (gaseous, liquid, or solid), secondly, the concentration of the conducting material must be fairly high, and, finally, the effect is not entirely reversible: the greatest conductivity jump is observed when the field is first applied.

In the literature of that period three views were put forward concerning the nature of coherers. Lodge[8-10] believed that the reason for the increase of the conductivity of the powder under the action of the field is the formation of a current-conducting path (bridge) due to the aggregation of particles under the influence of electrostatic forces; these forces "strip" insulating films from the surface of the particles, in particular oxide films. According to Auerbach[11], the role of the field is purely mechanical. The field induces a relative disposition of the particles such that it ensures a higher conductivity of the powder. By virtue of surface forces, the resulting structures are maintained also after the removal of the field. Branly[12-17] believed that the layers of insulating dispersion medium between the powder particles are "modified" on application of the field and become conducting.

The adhesion of the particles under the action of electrical pulses was confirmed by numerous investigators. Thus in his study, under the microscope, of the effect of electric discharges on copper, iron, brass, and silver powders, Arons[18] observed the formation of bridges from the powder particles. Particularly stable bridges were produced in copper powders. Sundorph[19] investigated iron and nickel powders. After the powders began to conduct current readily under the action of the field, he succeeded in isolating with the aid of a weak magnet a thin bridge connecting the electrodes. In Tommasina's experiments[20,21] bridges made up of metallic particles reached lengths of 20 cm in distilled water. Using horizontal electrodes, he observed the formation of a multiplicity of vertical chains of particles which immediately collapsed as soon as one of the chains reached the opposite electrode and closed the circuit. Thus the formation of conducting bridges in the powders was demonstrated experimentally.

The problem of coherers gave rise to a number of related problems. These include in the first place the problem of the breakdown in an electric field of aerosols and emulsions. Clark and Lodge[22] noted the common features of structure-formation processes in powders and aerosols in an electric field. The industrial methods for the removal of dust from air and dehydration of petroleum (Cottrell's method and others) originate from this phenomenon also.

Studies of the conductivity of natural air gaps are also closely associated with the problem of coherers. Harden[23] observed that, when a spark jumps in a discharge unit, certain particles are brought into motion in the 6 μm electrode gap and the process terminates in the formation of a bridge. This phenomenon was investigated in greater detail by Sundorph[24]. Using apparatus with movable electrodes, he observed the formation of bridges up to 50 μm in length in a constant field. Similar phenomena were later studied by Hoffman[25], Szèkely[26], Pearson[27], and Pectow[28]. All these studies confirm the characteristic structure formation under the action of an electric field in systems whose disperse phase is a product of the breakdown of the electrode.

At the beginning of the twentieth century coherers lost their practical value with the appearance of the Braun detector; they became of less interest, and studies in this field almost ceased. The literature on coherers has been reviewed by Aschkinass[29], Branly[17], and Righi and Dessau[30].

Starting with the 1920's finely dispersed systems began to attract attention to some extent as a consequence of the interest in problems of colloidal chemistry which arose at the time. The first investigations of the threadlike structure formed in the preparation of aerosol by the electric arc dispersion method were performed during this period[31-33]. Kuczynski[34], Muth[35], and Krasny-Ergen[36] investigated structure formation in emulsions in a high-frequency field. Kuczynski and Muth described the "construction" of chains from emulsion drops along the lines of force of the field. Krasny-Ergen calculated the minimum field strength necessary to overcome the thermal motion interfering with the organisation of drops into structures; his calculations agreed with Muth's experimental data. Pauli and coworkers[37,38] observed an increase of the conductivity of a gold hydrosol after prolonged passage of a current, due to the formation of chain structures.

Kruyt and Vogel[39] made a detailed study of structure formation in hydrosols in an alternating field. They studied gold, platinum, silver, copper, silver iodide, vanadium pentoxide, and paraffin hydrosols and also an aqueous emulsion of tetralin. According to their data, structure formation begins with the precipitation of particle aggregates on the electrode, after which branching structures, chains made up of particles similar to those observed in Pauli's experiments, grow from these deposits towards one another. When the chains are joined, the conductivity of the system increases by a factor of several tens. The higher the field strength the more rapid is the growth of the chains and the larger the gap between the electrodes which they can bridge. Under the microscope it is seen that the structured sol consists of a liquid traversed by a multiplicity of very thin intertwined and knotted threads forming a net-like structure. After the removal of the field the structure breaks down into individual fragments, consisting of many particles. The formation of chains is interfered with by bubbles produced, according to Kruyt and Vogel[39], as a result of the evaporation of water under the action of Joule heat. It was established, that on going from noble metals to copper, the capacity for the formation of threads falls. They rarely appear in copper sols and do not appear at all in silver iodide and vanadium pentoxide sols. In water–paraffin and water–tetralin systems the formation of bead-like aggregates from the dispersed dielectrics is again observed. Later the formation of similar structures was observed by Stauff[40], Us'yarov and coworkers[41-42] (in an alternating field), and also Pearce and Mech (in a constant field)[43]. Kruyt and Vogel distinguished bead-like structures (Perlschnurbildungen) formed from dielectrics and chains (Ketten) formed from metallic particles in accordance with the type of bond linking the units together: the bead-like structures broke down completely after the removal of the field, while the chains broke down into fragments consisting of many particles. According to Kruyt and Vogel, polarisation forces play a major part in the formation of chains; after the deformation and breakdown of the ionic shells of the micelles, van der Waals's cohesion forces begin to act. Subsequently recrystallisation processes develop at the site of direct contact between the nuclei, which accounts for the relative stability of the chains after the removal of the field.

We shall now consider the studies on aerosols performed during that period. These include primarily the work of

Beischer[44] on the stability of structures formed in aerosols of Fe_2O_3, ZnO, As_2S_3, NH_4Cl, iron, anthracene, and aminoazobenzene under the action of the field. The stability of these structures was determined from the maximum length of the chain formed in a field of about 300 V cm^{-1}, remaining attached to the electrode, without breakdown, after the removal of the field. The results were semiquantitative, since the true cross-sectional area of the chains was unknown. According to Beischer, the principal factor determining the stability is the adhesion of the particle aggregates. However, in some cases forces of a different type make a contribution: magnetic and electrostatic attraction forces (ferromagnetic aerosol of iron and the pyroelectric aerosol of aminoazobenzene) or crystal lattice bonding forces (ammonium chloride aerosol, which has a high vapour pressure at room temperature). Beischer regarded chains as tertiary formations. The primary formations are crystal nuclei and the secondary formations their spherical aggregates, which give rise to chains.

In his study of oil mists in an electric field, Winkel[45,46] failed to observe chain structures, a finding which in his view can be used to determine the state of aggregation of the disperse phase of aerosols.

Using the ultramicroscope, Artemov[47,48] studied the coagulation of the ammonium chloride aerosol in air of different humidities using a constant field. In the absence of moisture oriented branched aggregates are formed on the electrode. As the humidity increases, the aggregates grow in size and at 70% humidity drops of solution are deposited on the surface of the electrode instead of the aggregates. Artemov obtained similar results for anthraquinone and aminoazobenzene with water replaced by an appropriate solvent.

The coalescence of small droplets into larger ones is typical of mists in an electric field[49-51]. When the field is sufficiently strong, the drops are stretched into threads, which, on further increase of field strength, again break up into individual drops[52]. In many cases oriented coagulation of aerosols in an electric field takes place as a result of adsorption by the aerosols of the ions formed in air under the action of the field. Fuks[49] developed a theory of the aggregation processes in charged aerosols. Harvey et al.[53] described the formation of chain and three-dimensional network structures under the action of the field in silver and gold aerosols.

The studies on the breakdown of liquid dielectrics occupy a special place. It is known that the dielectric strength of transformer oil is lower the longer it is maintained under a potential. This phenomenon has been attributed for a long time to the aggregating effect of the field on the colloidal particles present and gradually accumulating in the oil. It has been shown in a number of studies that cellulose fibres are the most harmful in this respect, particularly in the presence of traces of water. While dry fibres lower the breakdown strength by 20%, moist fibres lower it by a factor of more than ten[54]. The explanation is that fibres which have adsorbed water are oriented along the lines of force of the field and form a bridge which is responsible for the breakdown. In the absence of fibres water has relatively little effect on the dielectric strength of the oil even when present at high concentrations.

Piper and coworkers[55] showed that, when an electric field is applied to the model phenol–liquid paraffin system, the electrical conductivity increases sharply as soon as a bridge structure consisting of acicular phenol crystals is produced.

At the beginning of the 1950's Frenkel', Gindin, Putilova, Moroz, and Shpanskaya published a series of papers on structure formation in disperse systems in a constant electric field. These studies originated from the problem of the corrosion of metals by liquid dielectrics. In the study of the mechanism of the corrosion processes in dielectrics it was found that the processes are electrochemical. It was established that electrochemical cells operate in hydrocarbon solutions of iodine or aliphatic acids and the current generated by them exceeds by several powers of ten the current which would be expected on the basis of the electrical conductivity of the initial solutions. To account for this phenomenon, it was suggested that salt bridges are formed between the electrodes during the operation of the cells, lowering thereby the internal resistance[56-58]. At the same time one of the present authors studied the suspensions of aluminium in kerosene as a possible reactive fuel and he decided to attempt to observe similar bridges in aluminium suspensions.

The first papers of the above cycle are in fact devoted to these suspensions. When a constant electric field is applied to a suspension of aluminium in petrol, the particles of the suspension begin to move, the rate of motion increasing with field strength E. Marked asymmetry of the motion is observed. Most of the aluminium particles are directed towards the cathode and cover the latter by a fairly thick layer of loose aggregates which grow in the direction of the anode. In the early stages of the process the latter remains clear. However, after a time it becomes coated by particles which have migrated from the cathode and which give rise to new aggregates growing to meet those formed earlier. Frequently the aggregates bound to the cathode suddenly break away from the latter and disintegrate into individual particles, giving the impression of small "explosions". At a certain stage of the process almost the entire space between the electrodes is filled by aggregates oriented along the lines of force of the field. Nevertheless the system is still a dielectric. However, when the field strength is increased to about 4000 V cm^{-1} (E_{cr}), electrical breakdown occurs and the system becomes conducting. This breakdown is readily observed from the sharp increase (by a factor of about 10^5) of the current in the circuit, the decrease of the field strength (from 4000 to 1 V cm^{-1}), and other effects. After the particles have fallen off, a single bridge in the form of a thin thread joining the electrodes is observed between them[59-61]. Subsequently the most important stages of the process were filmed[62,63]. Frame I in Fig. 1 shows the instant preceding the electrical breakdown. Frames II, III, and IV are pictures immediately after the breakdown associated with the formation of the bridge. The effects of the material and shape of the electrodes, the shape and size of the aluminium particles, and also the nature of the dispersion medium on the electrical breakdown were investigated[59-61]. If the bridges are not disconnected from the current source, they can exist for a long time. However, they persist even after the current has been switched off. The formation of the bridge and analysis of its behaviour suggest the presence of two types of bonds between its units. The first type is electrostatic and is observed in the stages of bridge formation preceding the electrical breakdown. The second type is a metallic bond produced at the instant of breakdown; by virtue of this bond the bridge continues to exist after the current ceases to flow. The voltage–current characteristics of the bridges[62,64] are in most cases monotonic up to the highest currents which the bridges can withstand. The initial sections of the characteristics are linear (Ohm's law holds) and then their angle of inclination to the E axis begins to decrease (the resistance increases) (Fig. 2, curve *1*). Such character-

istics are typical for metallic conductors whose temperature rises due to Joule heat.

The branches of the voltage–current characteristics obtained with rising (ascending branch) and falling (descending branch) voltage coincide in most cases (Fig. 2, curve *1*). However, sometimes this is not so (Fig. 2, curve *2*) and a characteristic hysteresis loop forms; this happens only when characteristic "flashes" occur on the current and voltage oscillograms, indicating a rearrangement of the structure of the bridges in the electric field. These and other observations confirm the hypothesis[60]

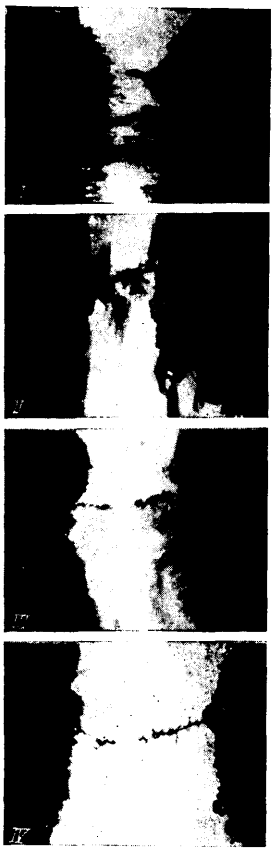

Figure 1. Film frames showing various stages in structure formation.

that the higher stability of the bridge conducting current compared with the bridge in the absence of current is due to the fact that, when the metal contact between the bridge unit breaks down, a fairly strong electric field arises and restores this contact. The bonds between the particles and the cathode, the formation of which is intrinsically responsible for the initiation of bridge formation, and the bonds between the particles themselves before electrical breakdown result from the electric polarisation of the particles. It must be emphasised that the aluminium particles are covered by thin layers of non-conducting oxide, which prevents the direct electrical contact of the particles with one another and with the electrode. Because of this, the suspension continues to be a dielectric even when the entire space between the electrodes is filled by the structures. The conversion of the system from a dielectric into a conductor occurs only when the electric field strength E reaches a value E_{cr} at which the insulating films in one of the numerous aluminium chains filling the space between the electrodes breakdown and the bridge becomes a metallic conductor. Hence follows the physical significance of E_{cr} as a measure of the breakdown voltage of the non-conducting oxide film, calculated over all the units of the bridge.

Indirect confirmation of the validity of this interpretation of E_{cr} is provided by the fact that suspensions of noble metals, for example platinum, become conductors at extremely low values of E.[65–68] Because of the very rapid precipitation of platinum particles, bridges of this metal, like those of aluminium, can be obtained only by "pulling" from the powder: a field of definite strength was established between the electrodes, after which the latter were allowed to touch the surface of a platinum powder; when the electrodes were raised, a bridge was drawn out. In contrast to the observations on the aluminium powder, the

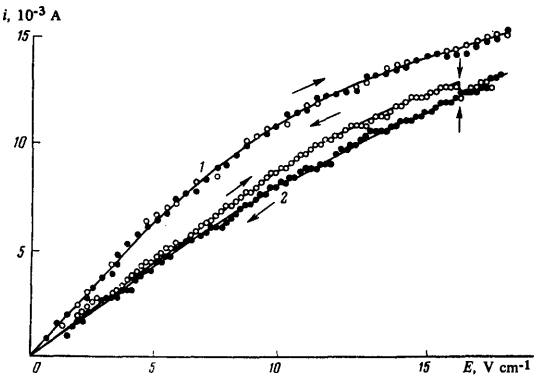

Figure 2. Voltage–current characteristics of the bridges.

platinum powder conducted current even at a minimal value of E. Evidently, it is sufficient for the platinum particles to be merely in contact with one another for the powder to behave as a conductor, since there are no bulk-phase oxide films on the surface of these particles.

Suspensions of copper, whose oxides are semiconductors, occupy an intermediate position between those of aluminium and platinum. Copper suspensions show an appreciable conductivity even at values of E much less than E_{cr} necessary for breakdown. As soon as the space between the electrodes becomes filled by structures made up of copper particles, a current appears in the circuit. A typical voltage–current characteristic for the system in this state is presented in Fig. 3, from which it follows that the conductivity of the system increases smoothly with field strength. Approximate calculations show that, when the overall field strength is only 100 V cm^{-1}, a field strength of the order of 10^4 V cm^{-1} is attained at the oxide film. Ioffe and Ioffe[69] showed that, for this value of E, the conductivity of Cu_2O increases exponentially with $\sqrt{E}$. In Fig. 3 the same relation is presented as a plot of ln σ against $\sqrt{E}$. Evidently the points lie on a straight line and therefore the relation holds in our case too. This

observation shows that before electrical breakdown we are dealing with conductivity due to the contacts between the individual copper particles when the conductivity of the system as a whole is determined by that of the surface semiconductor Cu_2O films on the particles. This is to some extent confirmed by the relation established between E_{cr} and the duration of oxidation of the copper powders

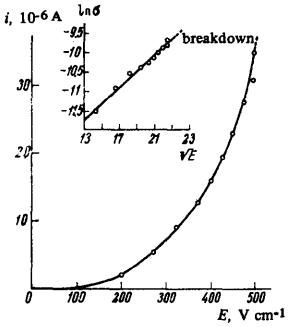

Figure 3. Electrical conductivity of suspensions and powders of oxidised copper before electrical breakdown.

(Fig. 4). The parabolic relation between these quantities is probably a consequence of the parabolic law governing the growth of oxide films. On the basis of this relation, one can set up rapid methods for the determination of the degree of oxidation of metallic powders (taking into account, of course, the characteristic features of the oxidation of each metal) [70].

Apart from the suspensions and powders of aluminium, platinum, and copper, dispersions of other metals have been investigated, namely of iron, cobalt, nickel, chromium, molybdenum, tungsten, antimony, bismuth, tin, lead,

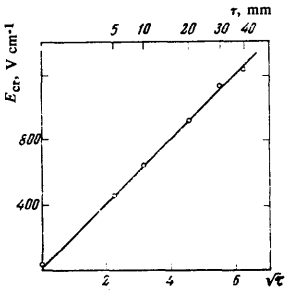

Figure 4. Variation of E_{cr} with the duration of oxidation of copper powders.

zinc, and silver. According to the behaviour of their disperse systems in an electric field, the metals can be divided into the following four groups:

1. Lead and bismuth. The suspensions of powders of these metals show some features resembling the dispersions of aluminium—almost complete absence of the conductivity of the structures before electrical breakdown.

2. Iron, cobalt, nickel, chromium, molybdenum, and tungsten. In their behaviour in an electric field, these metals resemble copper—weak conductivity before breakdown, increasing with E.

3. Tin and zinc. When an electric field is applied to suspensions of these metals, dendrite-like structures are produced, whose conductivity increases with the field even more than for the metals of the preceding group. However, the formation of a stable bridge and the electrical breakdown of the suspensions associated with it cannot be observed. Instead there is sparking with a crackling noise, accompanied by the evolution of gas bubbles—evidently products of the electrical cracking of the dispersion medium (petrol). The conductivity of the powders of these metals, due to the three-dimensional structure when $E \geqslant E_{cr}$, is replaced, like that of the metal powders of the preceding group, by the conductivity of the bridge; however, the electrical breakdown of zinc and tin powders, associated with the formation of a bridge, is not characterised so much by a jump in conductivity as by its stabilisation, i.e. the powders resemble cuprous oxide in this respect (see below).

4. Silver and antimony. Dispersions of these metals behave in an electric field in many ways similarly to the dispersions of platinum. The distinguishing features of these metals, like those of platinum, are a very low value of E_{cr} and the fact that no stable dendrite-like structures are formed in them. Although the problem requires further study (mainly quantitative), it is now clear that in general the behaviour in an electric field of the suspensions and powders of the metals investigated is determined by the nature, and in the first place by the conductivity, of their oxide films [71].

Suspensions of semiconductors such as boron carbide and cuprous oxide have also been investigated [65-68]. When a constant field is applied, the suspended particles of the carbide are deposited on the electrodes, preferentially on the anode. With increase in E, bridges begin to form in the space between the electrodes. As E rises, the number of such bridges increases, this being accompanied by a smooth rise of the current. When the apparatus is gently tapped, the bridges begin to fall off without disintegrating into smaller particles. On attainment of E_{cr}, the current increases sharply (by 2–3 powers of ten). After faulty, incomplete bridges have fallen out of the interelectrode space, a single bridge remains, which is responsible for the jump in the conductivity of the system; the form of this bridge is fairly characteristic: it is thin in the middle but thickens towards the ends attached to the electrode.

In cuprous oxide suspensions the formation of a bridge is also accompanied by a sharp rise of the conductivity of the system, but the attainment of E_{cr} is shown in cuprous oxide suspensions not so much by an increase of current (the latter increases only by a factor of two) as by its stabilisation.

Suspensions of soaps (the stearates of barium, zinc, nickel, cobalt, and copper and barium oleate) in aviation fuel and in liquid paraffin and also suspensions of a protein (egg albumin) in petrol have been investigated [65-68,72] in addition to the suspensions of metals and semiconductors. Outwardly the structure-formation processes in these systems are to some extent similar to those observed in suspensions of metals and semiconductors. When the cuvette with a suspension of soap and protein is included in a high-voltage circuit, the suspended particles begin to move rapidly. Then the particles of soaps (at $E = 7500$ V cm^{-1}) and hydrated protein form characteristic ribbon-like struc-

tures, the number of ribbons increasing with field strength. The formation of ribbons from protein begins at both electrodes but soap ribbons are produced predominantly from one electrode only; when the ribbons break away accidentally, their portions tend to migrate to the opposite electrode, where they become attached and initiate the growth of new ribbons. Sometimes the ribbons also grow in width, their edges coming into contact. The length of the ribbons reaches 1 mm and more, their width is 4–40 μm, and their thickness is of the order of 1 μm. The instant when the electrodes are joined together by the ribbons is shown by a sharp (approximately by 1–2 powers of ten) increase of the conductivity and a corresponding decrease of field strength. The study in polarised light of freshly prepared zinc stearate ribbons showed that they have an anisotropic structure, which, however, disappears after a time. When a field is applied to a suspension of dry albumin in petrol, the protein particles are drawn into the space between the electrodes and, becoming arranged along the lines of force of the field, form structures in which they do not adhere to one another but are merely in contact. It may be suggested that the conductivity of the ribbon-like structures from the soaps and the protein (under the usual dielectric conditions) is ionic and is of the surface and not bulk-phase type: in a later study[73] conductivity of this type was observed for lithium stearate suspensions in a mineral oil; it was explained by the presence of traces of moisture on the surface of the soap fibres.

Skanavi[74] noted that: "the suspension of a metal in a liquid dielectric constitutes to some extent a simplified model of a contaminated liquid. Therefore studies of this kind are not only of specialised interest, but they permit an approach to a more detailed examination of the problem of the mechanism of electrical breakdown and in particular the formation of conducting bridges or channels in contaminated liquid dielectrics... Before the electrical breakdown of a contaminated liquid containing conducting particles, a low-resistance bridge, joining the electrodes, is formed".

Similar views were later expressed by Kok and coworkers[75-80]. Incidentally, they suggested that, in order to enhance the dielectric strength of insulating oils, surface-active additives preventing the formation of bridges be used. They derived a relation between the "threshold" field strength at which the stable bridges are formed and the size of the colloidal particles of the admixture in the dielectric. The results of experiments on the electrical breakdown of liquid argon, nitrogen, and oxygen, proved to be close to the calculations.

Using the idea of the formation of conducting bridges from individual particles under the action of an electric field, Florek and Skowronski[81] constructed a discharge unit for the purification of liquid dielectrics.

Deinega and Vinogradov[82-85] investigated the effect of the electric field on greases—concentrated dispersions of soaps in mineral oils. They established that at the phase boundaries in these systems there exists an electrical double layer and that the sign and magnitude of the charges of the disperse phase and the dispersion medium can change under the action of surface-active substances and certain other factors. They observed that the particles of the disperse phase can have charges of opposite signs at the same time (electrical inhomogeneity, mosaic structure of phase boundary). If the disperse phase has charges of the same sign, then, after application of a constant field, a layer of dispersion medium forms near one of the electrodes; if the particles have charges of both signs, layers of dispersion medium are produced at both electrodes. In both cases the structural framework consisting of disperse phase particles undergoes elastic compression. At the same time the resistance of the grease to shear stress is reduced. The results of shear tests under conditions of steady flow of the grease are independent of the preliminary exposure of the latter to an electric field. Thus it was shown that the electric field induces reversible changes in the structure of greases, which in turn alter significantly their rheological properties.

We shall now review the studies of structure-formation in an electric field in suspensions of graphite and carbon black in dielectrics. It appears that the first study in this field was made by McDowell and Usher[86], who described the formation, under the action of an electric field, of chain-network structures from carbon black particles in toluene and other liquid dielectrics. The overall form of the structure-formation process in unstabilised carbon black suspensions is similar to that observed in noble metal sols[39], and therefore we shall not consider it. McDowell and Usher showed that the stabilisation of the suspension by the introduction of surface-active substances can reduce the capacity of the carbon blacks to form structures in an electric field.

Subsequently these systems were extensively studied by S. S. Voyutskii, V. A. Kargin, A. Voet, A. A. Bondi, and others†. In particular, the work of P. A. Rebinder and his school in the field of rheology and electrical properties of dispersed carbon blacks in liquid hydrocarbons must be mentioned. Voyutskii and Kargin with their coworkers[87] investigated conductimetrically the structure-formation in carbon black suspensions in a mineral oil. They believe that the observed increase of the conductivity of the system with temperature is due to an increase of the area of contact between the particles in the coagulation structures. Structure formation in graphite and carbon black suspensions in benzene, toluene, liquid paraffin, and kerosene under the action of an electric field was investigated by Yampol'skii[88]. When the structures are broken up by shaking or stirring, the mechanical strength and the electrical conductivity of the system are reduced sharply, but are gradually restored when the system is left at rest. The introduction of a surface-active substance (oleic acid, cetyl alcohol) greatly lowers the conductivity due to the growth of insulating adsorption-solvation shells on the surface of the graphite particles. Rebinder, Yampol'skii, and Wu Shu-ch'iu[89-91] investigated the behaviour of carbon black suspensions in liquid paraffin over a wide range of field strengths—from 0.025 to 500 V cm^{-1}. It was shown that the voltage-current characteristics of such systems are S-shaped: initially the conductivity of the system is constant, then it increases, and again tends to a constant value on further increase of E. These findings can be explained by a successive decrease of the thickness (breakdown) of the dispersion medium layers until at sufficiently high field strengths the thickest layers are penetrated. However, after electrical breakdown there remain extremely thin (about 10^{-7}–10^{-8} cm) residual layers of dispersion medium, which conduct current by a tunnel mechanism. Voet[92-98] and Bondi[99] hold similar views.

The combination of rheological and conductimetric studies on carbon black dispersions is of great interest. It has been established[89-91] that the stability of the structures to shear stress increases reversibly with field strength. The

† Here we are not concerned with studies of the electrical properties of carbon black dispersions in solid or highly viscous media (polymers) and in particular with the extensive series of studies on such compositions by B.A.Dogadkin, V.E.Gul', and their coworkers.

curves relating the electrical conductivity of the structured carbon black suspensions to rate of shear in an electric field are U-shaped, which can be explained by the effect of two competing factors: the decrease of conductivity due to the breakdown of the structures and its increase due to the increased frequency of collisions between the charged fragments of the carbon black chains[92-98].

This, in general, is the modern state of the problem of structure-formation in disperse systems in an electric field. In its further development the investigators will undoubtedly encounter the fundamental problem of the nature of the contact between the structural elements at various stages of structure formation. As mentioned earlier[61], the contact in stages preceding electrical breakdown (in the systems investigated by the present authors) is mainly due to forces associated with electrical polarisation, but, after typical breakdown, as in suspensions of aluminium, the particles are joined by metallic bonds (interatomic cohesion forces). However, the problem becomes complicated on going from metals to other substances, for example boron carbide: the question is whether the electrical polarisation forces at the instant of breakdown are weaker than adhesive forces or whether they are replaced by cohesive forces‡.

It is evident that very thin layers of dispersion medium between the elements of the structure always exist and their thickness depends on the lyophilicity of the disperse phase. However, as a result of the electrical breakdown, the particles are welded together and the dispersion medium layers undoubtedly disappear, but then the disperse structure ceases to be of the coagulation (reversible) type. Since before electrical breakdown many of the systems investigated exhibit appreciable conductivity, under these conditions the layers are so thin that they have little effect on the conductivity of the structure, either due to the tunnel effect or due to the breakdown of their continuity, particularly at lyophobic sites in the area of contact between the particles.

In conclusion we may note that structure formation in disperse systems in an electric field can be logically regarded as one of the aspects of the general problem of the formation of three-dimensional structures in disperse systems, which, as rightly pointed out by Rebinder, is one of the newest problems in modern colloidal chemistry. According to his classification[101-103], before breakdown the structures (at any rate those investigated by the present authors) are of the coagulation thixotropic type, but the role of electrical polarisation forces predominates. On the other hand, the structures produced after breakdown (bridges) are of the condensation (or crystallisation) type, but with the distinguishing feature that in the presence of a current the forces associated with the electric field constitute an additional stabilising factor for such structures.

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‡ The problem is closely related to the problem of electrical contact, which has been fairly thoroughly elucidated in Holme's monograph[100], for example.

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Radiolysis of Solid Inorganic Salts with Oxygen-containing Anions

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CONTENTS

I.	Introduction	61
II.	Radiolysis of nitrates	61
	1. Products of radiolysis	61
	2. Kinetics of radiolysis	64
	3. Mechanism of radiolysis	65
III.	Radiolysis of nitrites	66
IV.	Radiolysis of chlorates, bromates, and iodates	66
	1. ESR and optical spectra of irradiated salts	66
	2. Composition of stable radiolysis products	67
	3. Kinetics of radiolysis	67
	4. Mechanism of radiolysis	68
V.	Radiolysis of perchlorates	69
VI.	Annealing and interconversions of radiation-damaged regions	70
VII.	Relative stability to radiation in series of similar salts	70

I. INTRODUCTION

The extent and rate at which investigations have been made in the field of the radiation chemistry of solid inorganic compounds has been continuously increasing in recent years. The amount of information accumulated in the specialist literature on these problems is now very large. Data published up to 1962 were reviewed systematically by Sviridov[1], but there are no later reviews.

The aim of the present review was to arrange systematically and to discuss data on the radiation-induced reactions in the group of salts investigated in the greatest detail—alkali metal nitrates, nitrites, chlorates, bromates, and perchlorates. Particular attention has been devoted to the most recent investigations and the views formulated on their basis. Data published up to the end of 1966 are included in the review.

II. RADIOLYSIS OF NITRATES

Of all the inorganic salts with oxygen-containing anions, the nitrates have been investigated most vigorously, the study of alkali metal nitrates being the most detailed[2-11] and that of the nitrates of silver[2,12], alkaline earth metals[2,13,14], and lead[2,15-17] less so.

1. Products of Radiolysis

a. Optical spectra of irradiated nitrates. One of the first studies on optical absorption by irradiated sodium nitrate was that by Pringsheim[18]. At the temperature of liquid nitrogen an absorption band with a maximum at 335 nm was observed and at room temperature another band with a maximum at 355 nm appeared in addition. The author attributed the first band to an electron-excess centre and the second to NO_2^- ions. Absorption maxima at about 350 nm were also observed by Johnson[17] in the reflection spectra of irradiated potassium and lead nitrates. Cunningham made the most detailed study of this problem in the case of potassium nitrate[4]. Fig. 1, which is taken from his paper, shows the absorption spectrum of a potassium nitrate crystal irradiated at 4.2°K. In the range of doses less than 10^{20} eV g^{-1} six absorption bands were observed both at 4.2°K and at 77°K with maxima at 520, 355, 325, 290, 268, and 250 nm. The study of the behaviour of these bands on irradiation with light at a definite wavelength and on changing the temperature, and also comparison with the behaviour of ESR signals on treatment of this kind enabled the author[3,4] to identify these absorption bands. Thus the absorption at 250 nm was

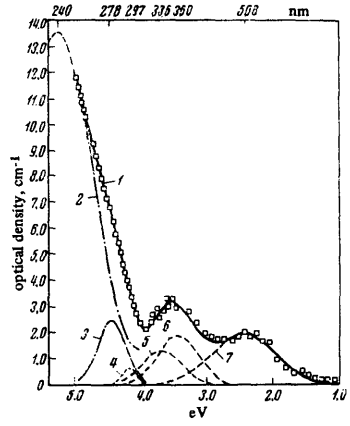

Figure 1. Optical absorption spectrum of potassium nitrate irradiated with γ-rays at 4.2°K;[4] the symbols denote experimental values; curve *1* was obtained by adding together curves *2–7*.

attributed to NO_3 radicals, that at 268 and 520 nm to NO_2^{2-} radical-ions, and that at 325 nm to NO_3^{2-}.

The centre responsible for the band at 290 nm, which is stable at the temperatures of liquid helium and liquid nitrogen, but is annealed on heating to room temperature, was not identified. Nor was the absorption band at 355 nm, which Pringsheim[18] attributed to nitrite ions, assigned.

However in a later study [19] Cunningham assigned this absorption band (*C*-centre) to the oxyhyponitrite ion $N_2O_3^{2-}$.

On irradiation of potassium nitrate with a dose in excess of 10^{20} eV g^{-1}, an additional absorption band was observed at 410 nm. Like the ESR signal[3] attributed to NO_2, which also appears at doses greater than 10^{20} eV g^{-1}, this absorption band was assigned to NO_2.

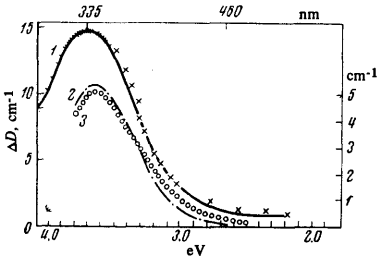

Figure 2. Light absorption by sodium nitrate [19]: *1*) irradiation with X-rays at 77°K for 75 min (right-hand scale); *2*) irradiation with γ-rays at 77°K for 30 min (left-hand scale); *3*) as for 2 after irradiation with $\lambda > 510$ nm light at 77°K for 40 min.

The spectrum of sodium nitrate [19] irradiated at 77°K was found to contain one absorption band with a maximum at 335 nm (Fig. 2). However, analysis of the shape of the curve and experiments involving bleaching with ultraviolet light enabled the author to identify two species responsible for this band (NO_2^{2-} and NO_3^{2-}) and to detect absorption at 410 nm, which is attributed to NO_2. It is interesting that

Table 1. Optical centres in irradiated nitrate systems.

Postulated absorption centre	λ_{max}, nm	Matrix	*T*, °K	Refs	Remarks
NO_3	250	KNO_3	4.2and77	4	Pulse radiolysis
NO_3	600,640,670	$H_2O + NaNO_3$	300	20	
NO_2	598,635,671	$Ce(NO_3)_4 + 6MHNO_3$		20	Flash photolysis
NO_3^{2-}	325	KNO_3	4.2and77	4	
NO_3^{2-}	335	$NaNO_3$	77	19	
NO_2	410	KNO_3	4.2and77	4	
NO_2	410	$NaNO_3$	77	19	
NO_2	400			20	
NO_2^{2-}	268,520	KNO_3	4.2and77	4	
NO_2^{2-}	335	$NaNO_3$	77	19	
NO_2^-	355	$NaNO_3$	300	18	
$N_2O_3^{2-}$	355	KNO_3	77	19	Stable up to 300°
NO_2^-	~350	KNO_3 and $Pb(NO_3)_2$	300	17	Reflection spectrum
$\bar{e}_{stab}$	335–340	$NaNO_3$	77and300	18	

Cunningham [19] observed an inhibiting effect by Ag^+ ions, introduced into the potassium nitrate and sodium nitrate lattices, on the increase in the intensity of the absorption bands assigned to nitrate ion conversion products.

Table 1 lists the optical centres in irradiated nitrates. For comparison, data obtained on the irradiation of liquid solutions of nitrates are included.

b. ESR Spectra of irradiated nitrates. The ESR signals in irradiated nitrates of potassium [3,5,7,21,22] and sodium [23–28] have been investigated in relatively great detail. There is also information about the ESR spectra of irradiated nitrates of silver [12] strontium [13,29], lead [16,29], and barium [29]. All the nitrates investigated were found to contain NO_2. NO_3 radicals were detected in potassium nitrate [3,5], sodium nitrate [25], and lead nitrate [16], and NO_3^{2-} species were found in potassium nitrate [3,5,21,24], lead nitrate [29], barium nitrate [29], strontium nitrate [13,29], and silver nitrate [12]. In the nitrates of silver [12], lead [29], and, to a slight extent, barium [29] the signal due to the unpaired electron is also split by the cations, i.e. in these nitrates the entire molecule and not only the anion serves as the electron trap. Therefore, especially in silver nitrate, the paramagnetic molecule $(AgNO_3)^-$ appears instead of NO_3^{2-}.

Table 2. Characteristics of the ESR spectra of the paramagnetic species in irradiated potassium nitrate single crystals

Postulated radical	*g*-Factor			Hyperfine structure constants, G			References	Remarks
	g_x	g_y	g_z	A_z	A_x	A_y		
1	2			3			4	5
NO	2.008	2.010	2.005	3.5	4.0	31	3	77° and 4°K
NO_2	1.9996	1.9932	2.0055	62.9	50.3	48.7	21	Formed on heating to room temperature between two exposures to radiation at 77°K or in the presence of potassium nitrite
NO_3		1.999			113		3	Potassium nitrate powder, dose 3×10^{20} eV g^{-1}
NO_3^{2-}	2.025	2.025	2.008	9	9	9	3	4°K, dose 3×10^{18} eV g^{-1}. Absent at 77°K; on annealing at 77°K for 2 h decreases by a factor of two
NO_3^{2-}	2.0057	2.0057	2.0015	63.4	31.8	31.8	5	77°K, dose 4×10^{19} eV g^{-1}, *H* parallel to *a*
NO_2^{2-}	2.006	2.006	2.002	61	32	32	3	4° and 77°K. Crystal axis *c* parallel to rotation axis and perpendicular to *H*
NO_3	2.006	2.006	2.001	0	0	0	3	4°K
NO_3	2.0232	2.0232	2.0031	4.3	3.5	3.5	5	77°K, rapidly decomposes at this temperature
O_2^-		1.958			0		3	Singlet. Appears on heating to 77°K or in measurements at 4°K on a crystal irradiated at 77°K

Furthermore, in silver nitrate there is also an ESR signal due to Ag^{2+} ions [12], the characteristics of which are not given in Table 4. The presence of NO, NO_2^{2-}, and O_2^- in irradiated potassium nitrate has been indicated only by Cunningham [3]. Thus different workers have identified different paramagnetic species in the same nitrate (potassium nitrate) and under the same or similar conditions. These discrepancies are illustrated by the characteristics of the spectra attributed to the paramagnetic species in irradiated potassium nitrate (listed in Table 2).

Although the ESR spectra of irradiated sodium nitrate have been studied in a number of investigations [23–28], only the spectrum attributed to nitrogen dioxide has been reliably interpreted. In two studies [25,28] NO_3 radicals have been identified in addition to NO_2. Table 3, which lists the characteristics of the ESR signals in sodium nitrate, shows that different spectra are attributed to NO_3 radicals. It has been shown [26] that the matrix has virtually no influence on the characteristics of the ESR spectrum due to NO_2. Therefore there is no doubt about the presence of NO_2 in other nitrates also, as can be seen from Tables 2–4. Certain contradictions in the identification of the individual paramagnetic species are readily seen from a comparison of the data in Tables 2–4.

1. If the spectroscopic characteristics of particular paramagnetic species remain the same or similar in the lattices of different nitrates (which probably in fact is the case), the ESR spectrum attributed to NO_2^{2-} in potassium nitrate by Cunningham[3], to NO_3^{2-} in potassium nitrate by Zeldes[22], to NO_3^{2-} in silver nitrate by Mosley and Moulton[12], and to NO_3^{2-} in potassium chloride containing nitrate by Jaccard[30] should be assigned to one of these paramagnetic species. This also applies to the interpretation of the spectra attributed to NO_3^{2-} in potassium nitrate by Cunningham[3] and in strontium nitrate by Zdansky and Sroubek[13] and to NO_3 species in potassium nitrate by Livingston and Zeldes[5] and in lead nitrate by Golding and Henchman[16]. This problem was examined in fair detail by Atkins and Symons[31]. On the basis of a comparison of the characteristics of these spectra with those of isoelectronic radicals, they assigned the first spectrum with $g_x = g_y = 2.006$, $g_z = 2.002$, $A_x = A_y = 32$–37 G, and $A_z = 61$–68 G to NO_3^{2-} radicals, and the second, with very slight splitting, to NO_3.

Table 3. Characteristics of the ESR spectra of sodium nitrate.

Irradiation temperature, °K	Paramagnetic species	$g_{\parallel}$ <111>	$g_{\perp}$ <111>	$A_{\parallel}$ <111>	$A_{\perp}$ <111>	References	Remarks
300	NO_2	2.0059	1.9982	48.0	58.4	24	
77	NO_2	2.0058	1.9964	50.5	59.1	26	
170	NO_2	2.0056	1.9966	51.1	58.4	27	
300	NO_2	2.0050	1.9970	53.0	57.8	27	
300	NO_2	2.006	1.9989	53	59	25	Disappears at 400°K
300	?	2.006	2.0097	0	0	25	ditto
300	?	2.0064	2.0147	0	0	25	Stable above 530°K
300	?	2.006	2.0237	0	0	25	Disappears at 400°K
77	NO_3	2.0004	2.0053	0	0	25	At 300°K converted irreversibly into three preceding species
77	NO_3	2.0022	2.0217	4.11	3.51	28	
77	?	2.0030	2.0225	0	0	28	

2. The spectrum which Cunningham[3] and Jaccard[30] attributed to NO radicals is assigned by Atkins and Symons[31] to NO_2^{2-} species. However, Cunningham[7] showed by chemical analysis and by the ESR method that NO species accumulate as the dose is increased. The two methods gave satisfactory agreement. The data are presented in Fig. 3. Because of this, and also in consequence of the very high anisotropy of the hyperfine splitting, Cunningham's view on this problem is probably more correct.

The identification of the radicals NO_3, NO_3^{2-}, and NO_2^{2-} requires additional investigations.

c. Composition of stable products. The generally adopted method for the determination of the final radiolysis products of nitrates involves the determination of the nitrite by diazotisation after dissolution of the irradiated nitrate in water. In the vast majority of cases the solutions of irradiated nitrates were analysed for nitrite only. In those studies where the gases evolved from the solution were analysed (see, for example, Refs. 2, 7, 19), it was shown that the gaseous radiolysis product is oxygen. The ratio $G(NO_2^-):G(O_2) \simeq 2$ is maintained in all cases, except for the initial stage in the radiolysis of lead nitrate[17].

However, it should be noted that there is a possibility of chemical reactions of the radiolysis products on dissolution of irradiated nitrate in water. Cunningham[7] showed that radical products such as O^-, NO_2, and NO may make a contribution to the yields of the radiolysis product determined as nitrite by the diazotisation reaction. On dissolution in water these products alter the concentration of nitrous acid by the following reactions:

$$O^- + H_2O \rightarrow OH + OH^-,$$
$$OH + NO_2^- \rightarrow NO_2 + OH^-,$$
$$2NO + O_2 \rightarrow 2NO_2,$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2.$$

Table 4. Characteristics of the ESR spectra of irradiated non-alkali metal nitrates.

Paramagnetic species	irradiated salt	g-Factor			Hyperfine structure constants, G			Refs	Remarks
		g_x	g_y	g_z	A_x	A_y	A_z		
NO_2	$AgNO_3$	2.009	1.9978	2.0039	50.7	48.5	69.6	12	Irradiation at 77°K. Intensity increases with disappearance of the Ag^{2+} signal on heating the crystal from 77° to 140°K
NO_2	$Sr(NO_2)_2$	1.9975	1.9975	2.0054	59	59	50	13	Room temperature. Formed at about 10^7 r or at about 10^5 r if the nitrate contains nitrite
NO_2	$Pb(NO_3)_2$	1.995	1.995	2.004	57	57	50	16	Room temperature
NO_3	$Pb(NO_3)_2$	2.029	2.029	1.998	1	1	2	16	ditto
NO_3^{2-}	$AgNO_3$	2.002	2.007	2.000	35.8	37.1	67.4	12	77°K. The unpaired electron is not localised at NO_3^-, but there is a hyperfine structure also due to the nucleus of the neighbouring cation
NO_3^{2-}	$Sr(NO_3)_2$	2.0081	2.0081	2.0027	0	0	0	13	Room temperature
NO_3^{2-}	$Sr(NO_3)_2$	2.0019	2.0060		68.8	37.3		29	90°K
NO_3^{2-}	$Pb(NO_3)_2$	1.9857	1.9912		66	36.5		29	
NO_3^{2-}	$Ba(NO_3)_2$	1.9997	2.0053		66.3	34.7		29	

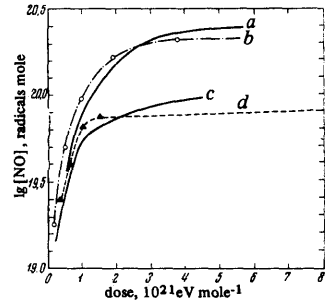

Figure 3. Formation of NO in potassium and sodium nitrates irradiated at 77°K:
a) and *c*) curves based on chemical analysis; *b*) and *d*) curves obtained by the ESR method[7].

It follows from this that $G(NO_2^-)$ determined by the diazotisation method includes the yields of other products: $G(NO_2^-) = G(NO_2^-)_{true} + \frac{1}{2}G(NO_2) + \frac{1}{2}G(NO) - \frac{1}{2}G(O^-)$. It can probably be regarded as established that the main radiolysis products at room temperature, at any rate for potassium and sodium nitrates, are NO, NO_2^-, NO_2, and oxygen. As shown by Cunningham[7], the presence of nitrogen in the gaseous radiolysis products noted by Hennig et al.[11] is a result of the desorption of air adsorbed on the surface of the nitrates during irradiation.

2. Kinetics of Radiolysis

Since nitrogen-containing radiolysis products of nitrates were determined by the diazotisation method in all the investigations except that of Cunningham[7], and since there are no data in the literature on the accumulation of all the decomposition products of NO_3^-, we shall henceforth examine the kinetics of the radiolysis of nitrates on the basis of the yield of nitrite, but one must remember that $G(NO_2^-)$ includes several components (see above).

a. Dependence of the radiochemical yield on the dose absorbed. This problem was investigated in greatest detail by Johnson and coworkers[2,32]. Using the decomposition mechanism for the nitrates of potassium, caesium, sodium, barium, lead, and silver,

$$MNO_3 \xrightarrow{h\nu} MNO_2 + O \quad , \tag{1}$$

$$O + NO_2^- \rightarrow NO_3^- \quad , \tag{2}$$

$$O + NO_3^- \rightarrow NO_2^- + O_2 \quad , \tag{3}$$

and applying the method of steady-state concentrations to atomic oxygen, they derived a second-order equation for the accumulation of nitrite:

$$a[NO_2^-]^2 + [NO_2^-] = bD \quad , \tag{4}$$

where a and b are constants for the given salt and D is the dose absorbed. Eqn. (4) describes satisfactorily the experimental data for caesium, sodium, barium, and lead nitrates (Fig. 4).

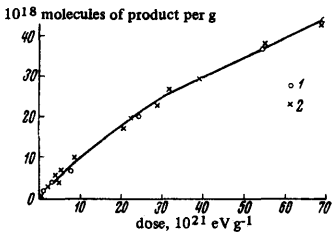

Figure 4. Formation of nitrite[2] in sodium nitrate: *1*) $[NO_2^-]$; *2*) $\frac{1}{2}[O_2]$; curve calculated from Eqn.(4).

From the above mechanism of radiolysis [Eqns. (1)–(3)], the following equation for the description of the accumulation of nitrite in potassium nitrate was obtained taking into account the changes in the concentration of NO_3^- ions[2]:

$$a \lg(1-\alpha) + \frac{\alpha}{1-\alpha} = bD \tag{5}$$

(where $\alpha = [NO_2^-]/[NO_3^-]_0$, a and b are constants, and D is the dose absorbed).

Cunningham and Heal[33], who used doses in excess of 10^{33} eV g^{-1}, described the kinetics of the radiolysis of potassium nitrate by the equation

$$\alpha = 1 - e^{bD} \tag{6}$$

where α is the fraction of nitrate decomposed, D the dose absorbed, and b a constant. A suitable equation for the kinetics of the radiolysis of silver nitrate could not be derived from the decomposition mechanism based on reactions (1)–(3).

The independence of $G(NO_2^-)$ of the dose for the individual nitrates, noted in numerous studies[1,8,10,17,34–36], is observed only for low doses, which are different for different nitrates. It is not difficult to see that all three kinetic equations [Eqns. (4)–(6)] degenerate at low doses to an expression of the form

$$[NO_2^-] = bD \quad , \tag{7}$$

which is consistent with the initial linear sections of the NO_2^- ion accumulation curves.

b. Effect of dose rate and LET†. The effect of dose rate on the radiolysis of nitrates has been investigated in numerous studies[10,33,35,37]. $G(NO_2^-)$ for the nitrates of potassium, sodium, caesium, and lead[37] was not found to change on varying the dose rate from 10^{17} to 10^{20} eV g^{-1} s^{-1}, as observed in other investigations[10,33,35] in the region of other dose rates and for other forms of radiation. The independence of the yield of nitrite of dose rate over a wide range (from about 10^{15} to 10^{20} eV g^{-1} s^{-1}) permitted an unambiguous interpretation of the results on the effect of the type of radiation on $G(NO_2^-)$. Table 5, taken from Hochanadel's paper[10], lists the values of $G(NO_2^-)$ obtained in the radiolysis of nitrates by different types of radiation. The similarity of the values of $G(NO_2^-)$ obtained

Table 5. Effect of LET on $G(NO_2^-)$ in nitrates[10].

Irradiated salt	3.4 MeV α-particles		^{60}Co γ-rays		44.5 keV X-rays	
	25°	120°	30°	150°	15°	150°
$LiNO_3$	0.7		0.02—0.2	0.03—0.4	0.02	
$NaNO_3$	1.3	1.1	0.27	1.0	0.4	1.1
KNO_3	2.2		1.5	3.0	2.0	3.0
$CsNO_3$	1.4		1.6	2.3	1.4	1.2
$Ba(NO_3)_2$	1.6		1.8	1.6	1.8	1.8

under the action of X-rays and γ-rays at 150°C and those obtained under the action of α-rays at 25°C led the author to the conclusion that thermal spikes are formed in the tracks of α-particles. The increase of the radiochemical yield of nitrite with increase in LET was attributed to a local temperature rise in the tracks of heavy particles. It should be noted, however, that it has been demonstrated quite recently that thermal spikes are not formed in the radiolysis of certain salts by protons[38].

c. The role of the cation. Even in the first studies on this problem, a definite relation between $G(NO_2^-)$ and the nature of the cation in nitrates was noted. The present generally accepted explanation is derived by considering the effect of the free space of the lattice on the probability of the reverse reactions. This problem is discussed in greater detail below.

d. Effect of other factors. The values of $G(NO_2^-)$ obtained by different workers show very appreciable discrepancies[1]. One of the possible reasons for the differences may be the different degrees of dispersion of

† Linear energy transfer (Ed.of Translation).

the nitrates irradiated[2,8]. The size of the crystals irradiated has a direct effect on the retention of gaseous radiolysis products within the lattice. On the other hand, the amount of gases retained influences the rate of the reverse reactions of the radiolysis products (see Section VI).

The influence of hetero-phase semiconductor oxide impurities[8] on the rate of radiolysis of potassium nitrate and sodium nitrate has also been investigated. Since the change in the rate of radiolysis under the influence of the oxides is correlated with the electron work functions of the latter, the effect of the additives on radiolysis was attributed to their donor-acceptor properties in relation to the nitrates. The decrease of the rate of radiolysis of sodium nitrate in the presence of Ag^+ ions in the sodium nitrate lattice was also attributed by Cunningham[19,34] to the acceptor properties of Ag^+. Accordingly, the introduction of Tl^+ ions, which, as shown by Boldyrev et al.[39] are electron donors, accelerates the radiolysis of potassium nitrate. Although the amount of experimental data is as yet insufficient to arrive at unambiguous conclusions concerning the mechanism of the effect of the admixtures, one may conclude that, like the degree of dispersion of the crystals, the purity of the salt irradiated has a significant influence on radiochemical stability.

3. Mechanism of Radiolysis

Although the nitrite ion accumulation curves are described satisfactorily by the kinetic equations based on reactions (1)–(3), the work of Cunningham[4,7,19,34] and the ESR spectroscopic data for irradiated nitrates, examined above, convincingly demonstrate a significantly greater complexity of both the primary and the secondary radiochemical processes in the irradiation of nitrates.

The primary processes must be regarded as ionisation and excitation processes:

$$NO_3^- \xrightarrow{h\nu} NO_3^-{}^*,\ NO_3,\ \bar{e} \qquad (8a)$$

$$M^+ \xrightarrow{h\nu} M^{2+} + \bar{e} \qquad (8b‡)$$

We may note that NO_3 can probably form not only as a result of reaction (8a) but also in the subsequent reaction

$$M^{2+} + NO_3^- \rightarrow (M^{+*} + NO_3) \rightarrow M^+ + NO + O_2\,, \qquad (9)$$

which is confirmed by the effect of the nature of the cation on the yield, noted above. Because of the high degree of excitation of the cation, reaction (9) probably does not stop at the stage where NO_3 is formed and continues to a more profound decomposition of the anion. The NO_3 radicals formed in reaction (8a) are unstable even at 77°K (at room temperature the presence of NO_3 is suggested only for lead nitrate[16]) and can decompose by the reactions

$$NO_3 \rightarrow NO_2 + O\,, \qquad (10a)$$

$$NO_3 \rightarrow NO + O_2\,, \qquad (10b)$$

or can serve as traps for thermalised electrons:

$$NO_3 + \bar{e} \rightarrow NO_3^-{}^* \rightleftarrows NO_2^- + O\,. \qquad (11)$$

Since the steady-state concentrations of NO_3 and thermalised electrons are insignificant, one may assume that reaction (11) is unlikely. Cunningham[3,7] found that NO is the primary product and NO_2 appears only for high values of the absorbed dose. It has also been stated in other papers[21,22] that NO_2 is a secondary product. Therefore reactions (10a) and (11) are unlikely, in contrast to reaction (10b). Since the electron affinity of NO_3 is greater than the energy of the N–O bond[40], the oxygen atom produced by fragmentation should have an excess kinetic energy of about 0.2 eV, if it is assumed that the energy associated with the electron affinity of the NO_3 radical is localised at a definite bond. On the other hand, in a solid the cage effect should be shown to the greatest extent. For these reasons, the excitation energy of $NO_3^-{}^*$ is often scattered by the crystal lattice and part of the $NO_3^-{}^*$ species break down into nitrite and atomic oxygen.

The secondary electron, thermalised in non-elastic collisions, may be stabilised in a trap of any type. Such traps may be the defects initially present in the lattice, ionisation products of the cation or anion, radiolysis products produced in secondary (see below) processes (O, O_2, NO_2, etc.), and finally normal lattice sites. In the last case it is reasonable to expect that in alkali metal and alkaline earth metal nitrates thermalised electrons are stabilised by anions and not cations, since the N^{5+}/N^{4+} redox potential is much higher than for M^+/M. Consequently the second primary product, in addition to NO_3, is electron-stabilised by anions[3-5,12,13,19,21,25,29]:

$$NO_3^- + \bar{e} \rightarrow NO_3^{2-}\,, \qquad (12)$$

but in silver nitrate, where the cation is an effective electron acceptor, we have $AgNO_3 + \bar{e} \rightarrow [Ag(NO_3)]^-$.

In potassium and sodium nitrates the absorption band and the ESR spectrum attributed to NO_3^{2-} vanish completely on heating the irradiated crystals to 300°K. At this temperature only the optical absorption bands attributed to $N_2O_3^{2-}$ and NO_2 are stable[4,19]. Consequently, apart from NO_3 radicals, species with an excess of electrons should make a contribution to the formation of the final radiolysis products:

$$NO_3^{2-} \rightarrow NO_2^- + O^-\,, \qquad (13)$$

$$NO_3^{2-} \rightarrow NO_2^{2-} + O\,. \qquad (14)$$

It is so far difficult to estimate the relative contributions to the yields of final radiolysis products by reactions (8)–(11) and (12)–(14). It is extremely probable that these two groups of reactions lead to different results. As already mentioned above, the relative importance of the individual reactions within each group is also different.

The present authors believe that steric factors should have a considerable effect on secondary processes involving the interaction of the products of reactions (8)–(14). Fig. 3 shows that the concentration of NO in sodium nitrate reaches a limiting value at a dose of only 1×10^{21} eV mole^{-1}, while in potassium nitrate the corresponding dose is approximately twice as high, the steady-state concentration of NO in sodium nitrate also being lower than in potassium nitrate. This shows that the reactions of NO depend on the lattice parameters. According to Cunningham, such reactions may be

$$NO + O \rightarrow NO_2\,, \qquad (15)$$

$$NO + O_2^- \rightleftarrows NO_3^-{}^* \rightleftarrows NO_2^- + O\,, \qquad (16)$$

$$NO + NO_3 \rightleftarrows N_2O_4^* \rightleftarrows 2\,NO_2\,, \qquad (17)$$

$$NO + NO_2^{2-} \rightarrow N_2O_3^{2-}\,, \qquad (18)$$

$$O + O = O_2\,. \qquad (19)$$

Reaction (17) occurs only in the presence of high doses, when there is a possibility of the formation of NO and NO_3 at adjacent sites[7].

‡ Here and henceforth M^+ denotes the normal cation (Na^+, K^+, Sr^{2+}, Ba^{2+} etc.) and M^{2+} an ionised cation, i.e. one which has lost another electron (Na^{2+}, K^{2+}, Sr^{3+}, Ba^{3+}, etc.). [See, however, the scheme on p.68, reaction (2c). (Ed.of Translation)].

The mechanism of the radiolysis of alkali metal nitrates examined above can probably be extended to the nitrates of alkaline earth metals. In the nitrates of heavy metals or variable-valence metals quite different electronic-ionic processes occur, whose importance is evident from the examination of the effect of impurities on the radiolysis of the nitrates[8,19,24,39].

III. RADIOLYSIS OF NITRITES

Alkali metal nitrites are extremely stable under the action of radiation[41]. The only products observed on irradiation of sodium nitrite are the paramagnetic species NO_2 and $N_2O_4^-$.[41-44] The signal detected after irradiation at 77°K (a strongly anisotropic triplet) has been attributed[42,43,45] to NO_2 molecules located in the *bc* plane of the crystal. These species disappear on heating the crystals to room temperature.

However, sodium nitrite irradiated at 20°C at doses of about 100 Mrad also gives a distinct ESR signal consisting of an anisotropic triplet on which a quintet is superimposed. It has been shown[41-44] that the first signal originates from NO_2 molecules in the *ac* plane of the crystal and the second is due to $N_2O_4^-$ ions formed as a result of the transition of NO_2^- ions or more probably NO_2 molecules into neighbouring cationic vacancies with rotation by 180° and formation of an N–N bond between these species and neighbouring normal anions. Optical absorption spectra in the visible and in the infrared regions[45-47] confirm this view.

IV. RADIOLYSIS OF CHLORATES, BROMATES, AND IODATES

1. ESR and Optical Spectra of Irradiated Salts

At the present time ESR spectra have been investigated in relatively high detail only for potassium and sodium chlorates irradiated with comparatively low doses ($< 10^6$ rad). The data concerning the signals from caesium and rubidium chlorates are extremely limited, while for bromates and iodates there is only a general indication of the possibility of detecting signals due to paramagnetic species in these salts and a brief description of the form of such signals in the spectra of powdered materials[48].

The ESR spectra of irradiated alkali metal chlorates are complex (Figs. 5 and 6). There exist different views in the literature concerning the interpretation of each signal in the spectrum (see Table 6). In later studies on the ESR spectra of irradiated sodium chlorate[49,54-56] it has been shown that at irradiation doses up to about 10^5 roengtens three paramagnetic centres are evident, their number increasing on further irradiation. The attention of the investigators has been drawn most to the complex signal, observed in almost all the studies, consisting of four anisotropic quartets.

Some workers[51,53,54] attribute this signal to the $ClO-ClO_3^-$ group, while Gamble[49] assigned it to ClO_3 radicals. The analysis of the signal in the latter study[49] shows, however, that its parameters (hyperfine structure and *g*-factor) differ appreciably from those of the spectra of ClO_3 captured in various matrices[50] and therefore the models of this centre proposed by Hasty[51] and Ramasastry et al.[52] must be preferred (see Figs. 5 and 6).

Studies of the ESR spectra at low temperatures (irradiation of crystals with fast electrons and recording of the spectra at 77°K) led to a new spectrum[50], which can be more definitely assigned to ClO_3 (Fig. 6). This radical proved to be extremely unstable; it breaks down on storage and under the action of light at 77°K after 35 and 15 min respectively.

The distinct central singlet in the spectra of irradiated chlorates has been attributed[52-54] to O_3^-. Probably this interpretation is correct, although it has been suggested[51,57,58] that the signal is due to the radical-ion O_2^-.

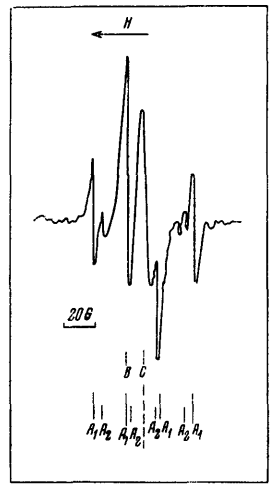

Figure 5. ESR spectrum of irradiated sodium chlorate (specimen irradiated and spectrum recorded at room temperature)[49]; A_1 and A_2–quartets due to splitting by ^{35}Cl and ^{37}Cl nuclei; *B* and *C*–singlets.

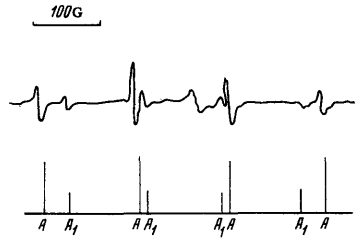

Figure 6. ESR spectrum of irradiated sodium chlorate (specimen irradiated and spectrum recorded at 77°K)[50]; A_1 and *A* as in Fig.5.

Table 6. *g*-Factors of the ESR signals from irradiated chlorates.

Radical				References
$O_3^-(O_2^-)$	ClO_3	ClO	ClO_3 / $ClO-ClO_3^-$	
g=2.00				51
g=2.0095	g=2.01	g=2.022 (position of the most intense line)	g=2.0023	52
	g=2.0102			53
			g=2.0085–2.009	49
g=2.0338			g=2.0124	54
	g=2.0033		2.003	55
	g=2.0032		2.0026	56
			g=2.0107–2.0135	50

The characteristic doublet observed in a number of studies has been assigned by all the investigators to ClO_2, the remaining lines of the ESR spectrum of this radical (it gives rise to a quartet) being masked by other signals which are in no way related to it. However, it should be noted that the parameters of this signal attributed to ClO_2 by Fayet and Thieblemont [55] differ from those found by Ramasastry et al. [52]

Apart from the identification of different species enumerated above, a number of investigators have observed in the spectra of chlorates irradiated at room temperature lines due to various unidentified centres [49,52,55]. The results obtained by Subbotin [54] show that the ESR spectra of the powdered salts irradiated at room temperature are qualitatively similar for all the alkali metal and alkaline earth metal chlorates. Data on the accumulation kinetics and the behaviour of the signals from a number of chlorates after annealing and on the relation between the rate of accumulation and the crystal lattice parameters were obtained for the first time [48,50] from the ESR spectra of alkali metal chlorates, the specimens being irradiated and the spectra recorded at 123° and 77°K. The irradiation of the salts at low temperatures with high doses (up to 10^8 rad) made it possible to obtain for the first time signals from bromates and iodates and to observe signals from potassium chlorate not detected previously. Nuclear quadrupole resonance signals due to ^{35}Cl nuclei in potassium and sodium chlorates have been described in certain brief communications [59-61]. The deformation of the lattices of these salts in the vicinity of the radiolysis products leads to the appearance of broad signals which have not been interpreted hitherto.

The information about the absorption spectra of irradiated salt layers of the type MXO_3 (X = halogen) are also extremely limited. Heal, who investigated the absorption spectra of thin single-crystal potassium chlorate plates irradiated with X-rays up to high doses (10^{23} eV g^{-1}), [62] established the presence in the spectra of three absorption bands—at 260 nm, 310 nm, and in the region of about 450 nm. By analogy with the positions of the absorption bands of oxychlorine anions in aqueous solutions (cf. Ref. 63), he attributed these bands respectively to ClO_2^-, ClO^-, and Cl_2O_6 and confirmed their presence by analysing the solution of the irradiated salt. In contrast to Heal's data, other investigators [52,64-66] observed only one band in the spectrum of irradiated potassium chlorate, with a maximum at 461 nm, which is stable at room temperature. When crystals irradiated with X-rays are exposed to light, an additional band appears at 340 nm (and at the same time also a new signal in the ESR spectrum), which has been attributed [65] to Cl_2^-. Under the same conditions, two absorption peaks, displaced towards the short-wavelength region of the spectrum, have been observed [64] in the spectrum of sodium chlorate.

A more detailed study of the colouring of sodium and potassium chlorates at room temperature [67,68] showed that in the spectrum of irradiated sodium chlorate there are three absorption regions: at wavelengths less than 260 nm and with maxima at 302–310 and 420 nm. The observed spectrum is believed [68] to consist of individual bands with maxima at 228, 260, 310, 360, and 420 nm for sodium chlorate and at 216, 260, 310, 360, and 450 nm for potassium chlorate. It is reasonable to assign the absorption at 260, 310, and 360 nm to ClO_2^-, ClO^-, and ClO_2 respectively. It is believed [68] that the absorption band at 216–220 nm is due to the transition of an electron from ClO_3^- to a lattice defect (analogue of the α-band in alkali metal chloride crystals), and the absorption in the region 420–450 nm is attributed to Cl_2O_6 and O_3^- or to simultaneous absorption by these species. The nature of the thermal and optical bleaching of the absorption bands studied in the same investigations [67,68] confirmed the hypothesis put forward concerning the structure of the absorption centres [67].

The models of the centres (enumerated above) responsible for the optical absorption in irradiated chlorates are the most likely. Apart from those described, there are, however, other hypotheses about the structure of the absorption centres [51,54].

2. Composition of Stable Radiolysis Products

In the first studies on the radiolysis of chlorates [64,68] the presence of oxygen, Cl^-, and ClO_2^- in the products was established. The composition of the radiolysis products was investigated in detail by Heal [62]. By analysing the solutions of irradiated potassium chloride and by absorption spectroscopy of the crystals, he determined the following stable products: O_2, Cl^-, ClO^-, ClO_2^-, ClO_4^-, and small amounts of Cl_2O_6 and ClO_2.

The initial radiochemical yields G_0 of the main radiolysis products of alkali metal chlorates and bromates based on the work of a number of investigators [69-77] are compiled in Table 7. Fig. 7 shows the accumulation curves for the radiolysis products of potassium chlorate [62].

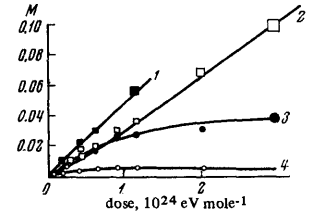

Figure 7. Accumulation curves for the main radiolysis products in potassium chlorate at room temperature [62]:
1) O_2; *2*) Cl^-; *3*) ClO_2^-; *4*) ClO^-.

Studies on the radiation chemistry of bromates [70-75] established that their irradiation in a nuclear reactor with mixed radiation (γ-rays, fast and slow neutrons) and with cobalt-60 γ-rays leads to the accumulation of the radiolysis products Br^-, Br_2, BrO^-, and BrO_2^-, i.e. the composition of the reduction products of bromate ions is similar to that of the products found in the radiolysis of chlorates. The products also contain O_2, but the presence of BrO_4^- has not been finally established. Chase and Boyd [78] also detected BrO^-, BrO_2^-, Br^-, O_2, and BrO_2 (the last tentatively) in aqueous solutions of alkaline earth metal bromates.

3. Kinetics of Radiolysis

A constant rate of accumulation of Cl^- and O_2 and a complex shape of ClO_2^- and ClO^- accumulation curves are characteristic of chlorates. Characteristic features of potassium chlorate, which has been investigated in greater detail, are also the insignificant effect of temperature in the range 77–300°K on $G(-ClO_3^-)$ and the probable formation of appreciable amounts of ClO_4^- or Cl_2O_6.

A group of studies on the Szillard–Chalmers effect in this class of compounds[79-81] is related to the investigations of the radiolysis of chlorates. Among the products in chlorates irradiated with neutrons, Cl^-, ClO_2^-, ClO^-, Cl_2, and ClO_4^- have been noted.

The radiolysis of alkali metal bromates has been investigated in greatest detail by Boyd and coworkers[72-75,82] (Table 7). The accumulation of Br^- is linear in the initial stage of the radiolysis (approximately up to 1×10^{23} eV g^{-1}); then it begins to take place with a gradually decreasing rate for all the bromates, except lithium bromate, the degree of deviation from linearity increasing in the series from lithium bromate to caesium bromate. In the temperature range 77–358°K the rate of radiolysis depends only very slightly on the irradiation temperature. The rate of accumulation of Br^- in caesium bromate is almost independent also of the irradiation dose rate.

One of the principal conclusions arrived at by Boyd et al.[72] is the correlation which they established between the "free space" in bromates and radiation stability. Such correlation holds also for a number of other inorganic salts[38].

Table 7. The yields of the main radiolysis products of salts of the type $MHalO_3$.

Irradiated compound	Products					References	Remarks
	G (Hal^-)	G ($HalO^-$)	G ($HalO_2^-$)	G (O_2)	G ($-HalO_3^-$)		
$NaClO_3$	2.14	—	—	—	—	76	α-Particles
$KClO_3$	0.4	—	1.2	1.57	—	64, 69	Room temperature, X-rays
$LiBrO_3$	0.13	0.21		—	0.23	72	Room temperature
$NaBrO_3$	0.88	0.64		—	1.48		
$KBrO_3$	1.07	0.46		—	1.53		^{60}Co γ-rays
$RbBrO_3$	1.02	0.82		—	1.85		
$CsBrO_3$	2.23	0.49		—	2.73		
Li^7BrO_3	—	—	—	—	0.47	74	Room temperature
$NaBrO_3$	0.59	0.22	0.59	—	1.4		Mixed reactor radiation
$KBrO_3$	0.63	0.20	0.54	—	1.3		
$RbBrO_3$	0.96	2.23	0.31	—	2.4		
$CsBrO_3$	0.61	—	—	—	3.4		
$LiBrO_3$	0.58	0.26	0.47	—	1.4		

Boyd[73] established that certain kinetic parameters of the radiolysis of lithium bromate under the action of neutrons differ from those which they described for γ-irradiation. In particular, the radiation yields are much higher (Table 7). For all the other bromates, the yields of products on γ-irradiation and irradiation in a reactor are very similar. The higher yield for lithium bromate is associated with the high efficiency of neutron capture by ^6Li nuclei. Thus, when mixed reactor radiation is used, the isotope composition influences the rate of radiolysis.

Among alkali metal bromates, the radiolysis of caesium bromate has been investigated in greatest detail[75]. Some information about the kinetics of product accumulation in the radiolysis of alkaline earth metal bromates has been published by Chase and Boyd[78] who noted a change in the yields with dose for all the products resulting from the secondary reactions involved in the thermolysis and annealing of the radiolysis products.

4. Mechanism of Radiolysis

The above data provide a basis for a mechanism of the radiation-induced decomposition of alkali metal chlorates. The following fundamental reactions are likely to occur in the radiolysis of the chlorates:

1. $ClO_3^- \xrightarrow{h\nu} ClO_3^{-*}$ → $ClO^- + O_2$, (a); → $ClO_2^- + O$, (b); → $Cl^- + {}^3/_2O_2$, (c); → $ClO + O_2^-$, (d); → $ClO_2 + O^-$, (e)
2. $ClO_3^- \xrightarrow{h\nu} ClO_3 + \bar{e}^*$, (a)
   $M^+ \xrightarrow{h\nu} M^{2+} + \bar{e}^*$, (b)
   $M^{2+} + ClO_3^- \rightarrow M^{3+*} + ClO_3^*$, (c)
3. $\bar{e}^* \rightarrow \bar{e}$, → $ClO_2 + O$, (a)
4. ClO_3^*, ClO_3 → $ClO + O_2$, → $Cl + O_2 + O$, (b)
5. $ClO_3 + e \rightarrow$ products 1a–1e (a)
   $ClO + ClO_3^- \rightarrow (ClO{-}ClO_3^-)$, (b)
6. $O_2^- + O \rightarrow O_3^-$, (a)
   $O_2 | \square a + \bar{e} \rightarrow O_2^- | \square a$, (b)
7. $O + O \rightarrow O_2$, (a)
   $Cl + Cl \rightarrow Cl_2$, (b)
8. $ClO_2^- \rightarrow Cl^- + O_2$, (a)
   $ClO^- \rightarrow Cl^- + O$, (b)
9. $ClO_2^- + O \rightarrow ClO_3^-$, (a)
   $ClO^- + O \rightarrow ClO_2^-$, (b)
10. $ClO_3^- + O \rightarrow ClO_4^-$, (a)
11. $ClO_3 + ClO_3 \rightarrow Cl_2O_6$, (a)
    $Cl_2O_6 + e \rightarrow ClO_3^- + ClO_3$. (b)

In the primary stage both excitation [reaction (1)] and ionisation [reaction (2)] of anions take place. The dissociation of excited ClO_3^{-*} species can result in the formation of various oxychlorine products [reactions (1a)–(1e)]. However, the formation of oxychlorine anions [reactions (1a)–(1c)] is more likely than reactions (1d) and (1e) because of the higher electron affinity of chlorine oxides compared with oxygen[40].

The following experimental findings confirm the occurrence of ionisation in chlorates: (1) the presence at low temperatures in irradiated sodium and potassium chlorates of a signal originating most probably from ClO_3;[50] (2) the formation on radiolysis of small amounts of Cl_2O_6 [76] produced as a result of bimolecular interaction between ClO_3 species [stage (11a)]. After the ionisation step, the excited electron loses its energy [the electron thermalisation stage, reaction (3)], and is then captured by a trap.

Reactions (2b) and (2c), the ionisation of the cation and subsequent conversion into M^{2+*} under the influence of the powerful field of the electron in the neighbouring anion, probably also occur. The excited radical ClO_3^* produced at the same time breaks down; among its possible decomposition products, only ClO_2 radicals have been observed so far.

In view of the high electron affinity of ClO_3 ($E = 3.96$ eV according to Ref. 40), the recombination of these species

[reaction (5)] can also lead to bond dissociation within the radical. The possibility of this occurring is largely determined by the ratio of the electron affinity of ClO_3 to the dissociation energy of Cl–O bonds in the chlorate. The latter is 2.38 eV in potassium chlorate [11]. The adoption of the $ClO–ClO_3^-$ pair as one of the paramagnetic centres in chlorates presupposes reaction (5b).

In the ESR spectra of irradiated chlorates one of the singlets has been assigned to the oxygen radical, which justifies the introduction of reaction (6a), but according to the latest studies stage (6b) is the more likely.

By analogy with bromates, one may assume that the annealing of the radiolysis products which occurs also in the radiolysis process itself at moderate and high temperatures involves both thermal conversion of unstable products [reactions (8a) and (8b)] and the reverse oxidation of oxychlorine products by atomic oxygen [reactions (9a) and (9b)] formed on decomposition of excited species [reactions (1), (4), and (5)].

It is at present difficult to determine the subsequent fate of the ClO_3 radicals formed in stage (2) (decomposition or dissociative recombination with an electron). However, the first data obtained on the thermal and optical bleaching of ClO_3 at low temperatures [50] suggest that reaction (5) is the more likely process, although reaction (11a) and the subsequent reaction (11b) are possible.

In view of what has been said, one might think that neutral oxychlorine radicals (ClO, ClO_2) and anions (ClO^-, ClO_2^-) are formed in chlorates by different reactions [reactions (2) and (4) and reactions (1) and (5) respectively]. Since the presence of the ClO_4^- anions in the radiolysis products of chlorates has been demonstrated in a number of studies and Sharman and McCallum [80] assert that ClO_4^- anions are formed by the further oxidation of chlorine in the chlorate anion, one must introduce tentatively reaction (10).

The formation of radicals and final products in the radiolysis of alkali metal bromates has been investigated in much less detail than for the chlorates. Only the problem of the accumulation of bromide and oxybromine anions with a low degree of oxidation of bromine has been adequately dealt with in the literature. The mechanism put forward [73,74] for the radiolysis of bromates appears to be less definite and justified than the set of fundamental stages which can be postulated for chlorates. It may be supposed (the comparison of the compositions of the molecular radiolysis products of chlorates and bromates confirms this) that the mechanism of the radiolysis of $MBrO_3$ is largely similar to that of the radiolysis of chlorates. The differences in the mechanism of radiolysis of these two groups of salts can be definitely established only by a thorough comparative study of the optical and ESR spectra of the salts.

V. RADIOLYSIS OF PERCHLORATES

The radical products of the radiolysis of potassium and ammonium perchlorates have been determined and investigated by the ESR method by a number of workers [83–90]. The presence of the paramagnetic species ClO_2 and O_3^- in potassium perchlorate irradiated at room temperature has been established [3,84] and certain kinetic characteristics of their accumulation and thermal breakdown have been determined [83]. By irradiating the specimens and recording the spectra at low temperatures, it is possible to observe two additional signals, one of which has been attributed [83] to O_3^-, while the other has remained uninterpreted. A study in the temperature range 77–100°K revealed two further ESR signals, which have been assigned tentatively to ClO_4 radicals [90].

The relatively stable ClO_3 and NH_3^+ species have been observed and definitely identified in irradiated ammonium perchlorate, while Boyarchuk et al. [85] also observed at low temperatures an unstable singlet which they attributed to electrons localised at lattice defects.

Among all the radicals enumerated, only the behaviour of NH_3^+ in ammonium perchlorate has been investigated in fair detail. The spectroscopic and kinetic characteristics of other paramagnetic centres have not been studied, nor have the ESR spectra of any other perchlorates. Optical absorption by radiolysis products in solid perchlorates has been investigated only for ammonium perchlorate [63,91]. Absorption bands with maxima close to 260, 300, and 360 nm, indistinct absorption near 420 nm, and absorption at wavelengths below 220 nm have been detected in the spectrum of ammonium perchlorate irradiated at 77° and 300°K. Comparison with the spectra of irradiated chlorates, aqueous solutions of the corresponding compounds, and the results of the analysis of the stable products of the radiolysis of ammonium perchlorate, led the authors to assign these bands to ClO_2^-, ClO^-, ClO_2, O_3^- (Cl_2O_6), and Cl_2^- respectively.

Heal [92] identified Cl^-, ClO_3^-, and O_2 as the stable radiolysis products of potassium perchlorate, after dissolving the irradiated salt in water. However, Baberkin et al. [69] have stated that the chloride appears only after heating the irradiated specimens above 370°K. Heal [92] has suggested the formation of hypochlorite and chlorite ions, whose presence in irradiated alkali metal and alkaline earth metal perchlorates was demonstrated later [93–96]—these studies showed that ClO_2 and metal oxides are also formed. The variation of the degree of accumulation of the main radiolysis products with the dose absorbed differs little from linearity. The deviations from linearity at high irradiation doses are due to secondary reactions involving the annealing and thermolysis of the products. The radiochemical yields of the radiolysis products of various metal perchlorates are listed in Table 8, which shows that the main radiolysis products of the perchlorates are chlorate and oxygen. The remaining products are formed with relatively low yields. It has been shown [93–95] that $G(-ClO_4^-)$ for potassium and sodium perchlorates is almost independent of temperature over a wide range of the latter.

Table 8. Radiochemical yields of the radiolysis products of perchlorates at room temperature.

Salt	$G(ClO_3^-)$	$G(ClO_2^-)$	$G(ClO_2)$	$G(ClO^-)$	$G(Cl^-)$	$G(O_2)$	$G(-ClO_4^-)$	References
$LiClO_4$	2.80	0.15	0.59	0.10	0.12	2.15	3.76	94
$NaClO_4$	3.57	0.17	0.11	0.09	0.42	2.96	4.36	94
$NaClO_4$	2.8	0.75	0.08	0.1	0.43	—	4.2	93
$KClO_4$	2.99	0.18	0.12	0.09	0.45	2.68	3.83	94
$KClO_4$	—	—	—	—	0.94	—	3.46	96
$RbClO_4$	4.06	0.20	0.12	0.14	0.75	3.84	5.27	94
$RbClO_4$	—	—	—	—	1.14	—	4.86	96
$CsClO_4$	5.28	0.22	0.10	0.17	1.07	5.28	6.84	94
$CsClO_4$	—	—	—	—	1.94	—	8.84	96
$Mg(ClO_4)_2$	4.29	0.14	0.07	0.03	0.15	2.62	4.67	94
$Ca(ClO_4)_2$	3.44	0.00	0.51	0.08	0.12	1.99	4.15	94
$Sr(ClO_4)_2$	3.90	0.19	0.14	0.11	0.19	2.61	4.58	94
$Ba(ClO_4)_2$	1.76	0.84	0.42	0.12	0.06	2.18	3.20	94

The relative content and the kinetics of the accumulation of stable radiolysis products, observed after dissolving irradiated ammonium perchlorate in water, differ from those quoted for alkali metal perchlorates. It has been shown[63,91,97,98] that the main radiolysis products are Cl^-, ClO_3^-, and Cl_2; the question of the presence of ClO_2^- and ClO^- in aqueous solutions of irradiated ammonium perchlorate remains open (see Table 9).

The accumulation of products is non-linear because of the thermolysis during irradiation (even at room temperature) of oxychlorine radiolysis products, but the overall yield $G(-ClO_4^-)$ in the radiolysis process remains constant. Attention has been drawn to the effect of LET on the yields of the radiolysis products[63,91].

The composition of the gaseous radiolysis products was established mass-spectrometrically only for ammonium perchlorate[63,99]. In irradiated crystals O_2, HCl, and N_2O retained by the lattice have been observed[99]—N_2O, NO, O_2, and H_2O are evolved from the crystals during radiolysis[63].

Table 9. Initial yields of the radiolysis products of ammonium perchlorate at room temperature.

Type of radiation	$G(ClO_3^-)$	$G(ClO^-+Cl_2)$	$G(Cl^-)$	$G(-ClO_4^-)$	References
200 kV X-rays	1.78±0.15	0.78±0.1	2.1±0.1	4.36±0.15	63
4.7 MeV protons	1. 8±0.1	1. 8±0.1	2.7	6. 8±0.15	91
^{60}Co γ-rays	1. 3	1.65	2.5	—	98

The post-radiative changes in the properties (mainly thermal stability) of ammonium perchlorate have been examined in a number of studies[100-105]. Stable final radiolysis products which catalyse thermal decomposition must probably be regarded as responsible for the increased rate of thermolysis of irradiated ammonium perchlorate. The data available at the present time on the composition and properties of intermediate and to some extent final radiolysis products are insufficient for the construction of soundly based mechanisms for the radiolysis of perchlorates at various temperatures. Therefore the mechanisms proposed for the individual intermediate stages of the radiolysis of perchlorates[63,83,91,94-96,106] must be regarded as tentative.

The principal postulates put forward in the construction of these mechanisms are as follows. It is suggested that the primary radiolysis products are mainly Cl^-, O_2, and ClO_3^-. The predominant formation of ClO_3^- as the primary product in the radiolysis of ammonium perchlorate has been pointed out[63,91]. Data on the effect of semiconductor impurities on the radiolysis of ammonium perchlorate[63,107,108] suggest that the products are formed on dissociative addition of an electron to ClO_3 and ClO_4 radicals. The important role of the interaction between the radiation and the cation, which leads to the formation of species with two and more positive charges, has been pointed out[106].

VI. ANNEALING AND INTERCONVERSIONS OF RADIATION-DAMAGED REGIONS

A number of investigators have undertaken, particularly in recent years, the study of processes involved in the restoration of the properties and the stoichiometric composition of irradiated materials, under the influence of various factors on the irradiated compounds. Frequently in studies of this kind thermolysis and interconversions of the radiolysis products are observed together with the intrinsic annealing. Studies in this field consist of two groups in each of which the problem is formulated in a slightly different way.

Most of the investigations deal with the study of the annealing phenomena in preparations (mainly inorganic oxygen-containing salts stable to radiation) irradiated with slow neutrons. Problems concerning isotope separation using the Szillard–Chalmers effect and the time-variation of isotope distribution between the individual chemical species in irradiated materials have been mainly examined (for reviews, see Refs. 109–111).

A comparatively small number of publications concern the changes in the concentrations of the radiolysis products in solid salts during post-radiative annealing. Most of these studies have been carried out on potassium nitrate and certain heavy metal nitrates. The available literature data are concerned almost exclusively with the kinetics of thermal annealing[10,14,15,38,94,112-118], while the post-radiative changes in the products under the influence of other factors have been investigated very little.

Annealing in nitrates is regarded approximately as the oxidation of nitrogen–oxygen products (mainly NO_2^-) by radiolytic oxygen[112,113]. The rate and extent of this process are significantly influenced by all types of treatment of the salt: pressing[113,114,116], grinding[115], introduction of heterovalent ions into the lattice[39]. Annealing is greatly accelerated at the polymorphic transition temperatures[117]; in some nitrates it appears to involve a more complex mechanism than simple oxidation of NO_2^- by oxygen trapped in the lattice. There must be various mechanisms of the effects of the preliminary treatment on thermal annealing[114,115].

Among cases of non-thermal annealing, a decrease of the amount of radiolytic NO_2^- in lead nitrate on pressing[114] and irradiating the preparation with ultraviolet light has been observed.

Unstable radiolysis products of oxyhalogen salts can also undergo changes during annealing of the irradiated compounds[72,75,76,94,119-121]. According to some investigators[72,75,111,121-123], two groups of reactions then occur–recombination of oxychlorine or oxybromine products with oxygen (i.e. the intrinsic annealing) and their thermolysis to the chlorides. In alkali metal and alkaline earth metal bromates these reactions take place during the irradiation process itself even at room temperature and result in variable yields of the products during radiolysis.

VII. RELATIVE STABILITY TO RADIATION IN SERIES OF SIMILAR SALTS

It has now been firmly established that the stability of inorganic compounds (including oxygen-containing salts) to radiation is determined both by their macroproperties, in particular the structural and energy properties[94-96], and the nature and type of damage to the crystal lattice[107,124].

One of the most clearly established relations between stability and macroproperties of similar salts is that, on substitution of the cation in series of salts with the same anion, the radiation yield of the products changes smoothly and in parallel with the variation of the most important characteristics of the crystal lattice ("free space" and lattice energy, electronic fraction of the ions, etc.). The study of relations obtaining in radiolysis in series of similar compounds over a wide range of temperatures[48,50,125]

and in the annealing of nitrates [118] and also the study of the radiolysis of aqueous perchlorate systems [106] permit a more detailed examination of this problem. In particular, three temperature regions may be isolated in which the origins of stability series and the very nature of the relations obtaining in series of compounds may be different.

At low temperatures (77°K) the accumulation in alkali metal bromates and chlorates of radical products of the ionisation of anions takes place with a yield which increases in the series in parallel with the increase of the electronic fraction of the anion [50]. At the same time other radicals, whose yield increases in the opposite sense, i.e. in parallel with the increasing electronic fraction of the cation and the "free space" in the lattice, become stabilised under these conditions.

At higher temperatures (between 120° and 150°K) the radicals of the first type disappear, while the yields of those of the second type increase. Probably, starting with the above temperatures, the overall rate of accumulation of products in series of compounds with a variable cation or anion (for example, in the second case in the series $KClO_3$–$KBrO_3$–KIO_3) increases in parallel with increasing "free space" and electronic fraction of the cation. A similar relation is also observed in the accumulation of final, molecular radiolysis products, which are analysed chemically.

Similar relations (as regards stable products) have been established by a number of workers for alkali metal and (in a number of cases) alkaline earth metal halides, azides, nitrates, chlorates, bromates, perchlorates, and permanganates [38,50,78,106,126] and they are probably common to inorganic salts irradiated close to room temperature. Until recently it has been assumed that the direct origin of series relations of this type is associated with the change only in the *"free space" of the crystals* in the series of salts. As the "free space" increases, the cage effect and the probability of the reverse reactions of the intermediate radiolysis products decrease, which in fact entails an increase of the radiation yields of the products.

However, recently it has been suggested that the change in "free space" cannot be regarded as the only origin of related series in the temperature range investigated. According to some investigators [3,4,93,106], the interaction between radiation and the salt cations must make a significant contribution to the yields of the radiolysis products. This view was confirmed experimentally for the first time for silver nitrate and alkali metal perchlorates by Mosley and Moulton [12] and Wang Wen-hsin et al. [106] respectively. The interaction between radiation and cations which takes place with a probability proportional to the electronic fraction of the latter leads to the formation of additionally ionised cations (mainly M^{2+}), whose coulombic field may be sufficient to remove an electron from a neighbouring anion [106]. The energy evolved on addition of an electron to M^{2+} may result in the decomposition of neighbouring radicals and anions.

Finally, in radiolysis at elevated temperatures (different for different salts) it is desirable to take into account the effect of annealing processes, occurring during irradiation, on the yields of products and the occurrence under these conditions of radiation stability series. According to Zakharov et al. [118], the rate and extent of annealing in alkali metal nitrates increase appreciably in the series ranging from sodium nitrate to caesium nitrate, which means that they vary in parallel with the increase of "free space", i.e. with the improved conditions for the diffusion of radiolysis products. The activation energy for the annealing in nitrates is much higher than the activation energies for the processes occurring in radiolysis. Therefore the variation of radiation stability in series of these salts at elevated temperatures must be less pronounced and possibly (if not prevented by thermolysis) actually the reverse of the variation of radiation stability at low temperatures [118].

The rates of annealing (re-oxidation) and thermolysis of the oxyhalogen products in perchlorates, chlorates, and bromates also depend on the "free space" [78,94]. This must affect the radiation stability series for the salts at elevated temperatures.

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Autocatalytic and Impedance Phenomena and the Effect of the Physical State of the Solid Product on the Acceleration and Retardation of Reversible Topochemical Reactions with Participation of Solid and Gaseous Reactants

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CONTENTS

I. Introduction 73
II. The mechanism of autocatalysis 74
III. Catalysis by a solid product 78
IV. The impedance phenomenon 80
V. Unblocking of the initial solid phase 81
VI. The Pilling-Bedworth rule and the principle of the acceleration or retardation of reversible topochemical reactions with participation of gaseous and solid reactants 82

I. INTRODUCTION

During the last 2–3 decades significant advances have been made in the chemistry of solids [1–16]. However, it is noteworthy that many problems of the kinetics and mechanism of heterogeneous reactions involving solids are only in the initial stage of development. Furthermore, the development and research in this field and the accumulation of experimental data make it necessary to revise or correct the classical hypotheses in this branch of science.

The present review deals with the most important kinetic features of reactions of the type

$$A(solid) + C(gas) \rightleftarrows B(solid), \quad (1)$$

$$A(solid) + C(gas) \rightleftarrows B(solid) + D(gas). \quad (2)$$

Reactions of the first type include the formation of metal oxides, sulphides, selenides, and halides, the hydration of oxides and their conversion into carbides, and the reverse reactions. Processes of the second type include numerous reactions involving the reduction of oxides to the metals by gaseous reducing agents and the reverse reactions, as well as certain other interactions. Reactions (1) and (2) are heterogeneous and take place at an interface. Therefore the physical state and the topography of the surface of the initial solid phase A and the product B play a very important role in the kinetics of these processes.

The intrinsic chemical step is complicated by a number of physical phenomena which accompany it: the rearrangement of the crystal lattices of the interacting phases and their recrystallisation and sintering, the diffusion of the reactant C and the product B in the gaseous medium and their motion through pores and cracks in the solid phases A and B, the adsorption and desorption of gases, and the supply and removal of heat. Therefore the processes can take place both under kinetic and diffusion-dependent conditions.

In the examination of the kinetics of reactions (1) and (2) under isothermal conditions (this is the case most frequently encountered in technology), we shall distinguish two factors which have been called "autocatalysis" and "impedance".

Autocatalysis consists in the reaction, having begun after a certain induction period, developing at an increasing rate, the process gradually coming to a stop only at more advanced stages as a result of the disappearance of the initial reactant. The accumulation of the product of an autocatalytic reaction can be described graphically by an S-shaped curve and mathematically the relation between the extent of reaction α and time t can be expressed by the Kolmogorov–Erofeev equation, for example [17]:

$$\alpha = 1 - \exp(-kt^n). \quad (3)$$

The self-acceleration of the reaction and a rate maximum on the kinetic curve have been observed experimentally in numerous investigations [18–27].

Another no less interesting feature of reactions (1) and (2) is that the formation of the product B results in the separation of the reactants in space and the appearance of factors hindering the process, whose magnitude increases as the solid product accumulates. This phenomenon has been called impedance. Factors hindering the reaction can arise even at the very beginning, whereupon the rate will steadily decrease (provided, of course, that there are no abrupt changes in the nature of the process itself, the

conditions of the process, or the physical state of the interacting phases). The time-dependent inhibition of the process can be described mathematically either by a parabolic or a logarithmic relation[28,29]:

$$\delta^n = kt, \tag{4}$$

$$\delta = \ln(kt), \tag{5}$$

where δ is the thickness of the layer of product, t the time and n the exponent of the parabola.

Despite the abundance of the available experimental data, the nature and mechanism of autocatalysis have not yet been completely elucidated. In the literature there are contradictory interpretations of this phenomenon[30-33]. The occurrence of extrema on the kinetic curves can be explained in different ways[13]. The extensive experimental data on impedance have not been adequately systematised.

The aim of the present review is to reveal certain contradictions in the interpretation of the mechanisms of autocatalysis and impedance. The comparison of these phenomena in a single review should facilitate a deeper understanding of their nature and mechanisms. Analysis of the experimental data which have accumulated in this field during the last decades permits the formulation of an empirical principle broader than, for example, the Pilling–Bedworth rule[34] which has existed since 1923.

II. THE MECHANISM OF AUTOCATALYSIS

Usually the acceleration of reactions (1) and (2) is attributed to the increase during the process of the area of the A–B interface. According to the theory of the initiation and growth of a new phase developed by Gibbs, Volmer, Frenkel', Roginskii, and others, it is now believed that, after the formation of the nuclei of the new phase B, further reaction is localised at the interface between the phases A and B.[35] The process develops from the nuclei into the bulk of the specimen. Todes gave a mathematical description of this mechanism. If the particle is very small, the nucleus can completely fill it up before the second nucleus is produced—this is a case of mononuclear transformation in a chemical reaction[36].

Clearly reactions of types (1) or (2) extend into the bulk of the compact crystal, having begun on its surface. However, the theoretical foundations of the role of the A–B interface in autocatalysis, and the details of the model of this surface and its application to any type of topochemical reaction have given rise to a number of contradictions and therefore they require revision and correction. For example, Esin and Gel'd, gave the following explanation of the role of the A–B interface, on the basis of Langmuir's studies, in connection with the discussion of the mechanism of the reduction of an oxide to the metal by a gaseous reducing agent[37]. It is assumed that in the reaction

$$a\mathrm{A(solid)} + c\mathrm{C(gas)} \rightleftarrows b\mathrm{B(solid)} + d\mathrm{D(gas)} \tag{6}$$

the rates of the forward (V_1) and reverse (V_2) processes depend on the total areas of the solid phases:

$$V_1 = k_1 S_A p_C^c, \tag{7}$$

$$V_2 = k_2 S_B p_D^d. \tag{8}$$

On attainment of equilibrium, $V_1 = V_2$ and

$$k_1 S_A p_C^c = k_2 S_B p_D^d, \tag{9}$$

whence

$$K = \frac{k_1}{k_2} = \frac{S_B p_D^d}{S_A p_C^c}. \tag{10}$$

It follows from Eqn. (10) that the equilibrium constant K depends on the ratio of the total areas of the solid phases, but this is inconsistent with experiment.

To eliminate this "contradiction", Esin and Gel'd[37] conclude that the reactions of the gases C and D with the solids A and B do not take place on the entire surface of each phase but only at their contact boundary. They believe that such localisation of the process in a narrow contact zone between two solid phases has a number of advantages.

However, one should bear in mind that the appearance of a solid product can give rise to diffusion-dependent inhibition and can result in a change of the process conditions from kinetic to diffusion-dependent. Then the kinetic laws should cease to apply and should be replaced by diffusion laws. The application of the law of mass action to reactions of types (1) and (2) in its usual kinetic form is possible only when the interaction of the gas with solid phases is not complicated by either external or internal diffusion. This means that the gas phase is mixed sufficiently vigorously and has free access to the surface of the solid reactant, i.e. the supply of the molecules of C and D to the substances A and B is not rate-limiting.

Furthermore, one should bear in mind that, as equilibrium is approached, the difficulties associated with the formation of the new phase become increasingly significant. The size of the critical nucleus is inversely proportional to the degree of chemical supersaturation raised to the third power. This means that at equilibrium the fundamental forward and reverse steps (for example, oxidation and reduction) can take place on both surfaces (A and B) without the formation of a new solid phase.

This conclusion becomes particularly convincing if the following version of equilibrium is postulated. We assume that the reaction volume contains the solid phases A and B, which are separated in space, and that the gas mixture (C + D) has the equilibrium composition. Clearly in this case there is no A–B interface but a dynamic equilibrium nevertheless exists.

Therefore one can assume that at equilibrium the reaction surface is not the A–B interface but the surfaces of the phases A and B (for example an oxide and a metal) which are accessible to the gas. Since on attainment of equilibrium the number of forward reaction steps becomes equal to the number of reverse steps, it must be assumed that the reaction surface areas S_A and S_B are equal regardless of the ratio of the total areas of the phases A and B:

$$S_A = S_B \tag{11}$$

Here by S_A and S_B we understand not the macroscopic areas of the phases A and B but those surfaces of both solid phases on which the forward and reverse reaction steps can take place. It is possible to explain in this way the independence of the equilibrium constant for the topochemical reaction of the ratio of the surface areas of the solid phases. Therefore the explanation by Esin and Gel'd[37] of the role of the A–B interface in autocatalysis is not very convincing.

For processes which are the reverse of reactions of type (1) (thermal dissociation processes), Jacobs and Tompkins give the following explanation of autocatalysis[38]. The Gibbs free energy (ΔG) of formation of a nucleus of the new solid phase A must include not only the difference between the thermodynamic potentials of the products and reactants ($\Delta G'$) but also the energy γ of the strain in the crystal lattices of the solid phases at the sites where they are in contact. Accordingly, the following equation holds:

$$\Delta G = m\Delta G' + \sigma\gamma \tag{12}$$

where σ is a geometric factor (equal to $4\pi r^2$ for a spherical

interface) and m the number of molecules involved in the formation of the nucleus. Eqn. (12) can be put in a different form:

$$\Delta G = am^{2/3} - bm . \quad (13)$$

Here a is proportional to the strain energy and b denotes the free energy change per molecule with the sign reversed.

If $\Delta G' < 0$, ΔG is a decreasing function of m when $\gamma = 0$ or there is a maximum when $\gamma > 0$ (Fig. 1). The maximum value of ΔG corresponds to the critical size of the nucleus (m_{cr}). Apparently as a result of the strain due to the formation of the new phase, small particles of A are unstable and tend to be reconverted into B, while large particles are more stable in relation to the reverse transition. Jacobs and Tompkins[38] believe that because of this subsequent reactions take place preferentially at the interface between the two solid phases and not via the formation of a large number of submicroscopic particles A. The phase A formed in the reaction steadily increases in size, extending from the nuclei into the bulk of the crystal.

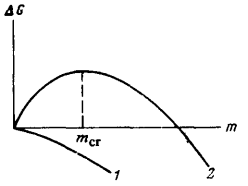

Figure 1. The ΔG–m curve for $\Delta G' < 0$: *1*) $\gamma = 0$; *2*) $\gamma > 0$.

The authors explain the autocatalytic nature of the reaction by a general hypothesis, according to which the nuclei are formed initially, this being followed by a period of their relatively rapid growth. If the activation energy for the growth at the interface is less than the activation energy for the formation of the nucleus, then the growth of the already existing nuclei predominates over the formation of new ones and the phase formed acquires the form of individual compact grains. In the opposite case a large number of very small nuclei are formed, none of which attains a size sufficient for observation with the naked eye.

The above mechanism of the development of the process differs little from the classical hypotheses of Volmer and Frenkel'[39,40]. It has the advantage that it can embrace in a general form a wide range of topochemical reactions, including reactions (1) and (2). At the same time it is readily seen that a more concrete application of the theory to reactions (1) and (2) requires the correction of some of its postulates. This applies in particular to the structural model of the A–B interface and the question of the site where the reaction takes place.

Autocatalysis due to the growth of the A–B interface requires in the first place that such an interface be present. However, it is known that, with the exception of molecular crystals, most solid crystalline chemical compounds exhibit appreciable deviations from stoichiometry (see, for example, Ref. 41). Furthermore, there is a possibility of the occurrence in the process itself of unstable transitional structures which, from the thermodynamic point of view, can be embraced by the concept of the solid solution. Therefore there may be no definite interface between the solid phases.

Furthermore, the volumes of the interacting phases are not as a rule equal. Because of this and because of the difference in the rates of migration of the elementary species through the layer of the solid products, the solid phase formed is usually very porous, amorphous, or finely dispersed. In this connection, it is interesting that as early as 1940 Erofeev examined photographs of nuclear grains and found that crystallisation processes are separated in space from the interface. An amorphous product, which becomes crystalline only at a certain distance from the contact surface, is in contact with the initial substance. In some cases the solid crystalline product is not observed at all or is observed only a considerable time after the reaction. Thus the crystallisation process is separated from the intrinsic chemical reaction both in space and in time[17].

If the volume of the new solid phase is smaller than the volume of the initial solid consumed in the formation of the former, then, if the process takes place under conditions which impede sintering and recrystallisation, the reaction usually results in the formation of a finely dispersed porous product. Thus the reduction of single-crystal and polycrystalline oxides by gaseous reducing agents can yield pyrophoric metal as the product[42]. The dissociation of calcite, $CaCO_3 \rightarrow CaO + CO_2$, leads to the formation of a product which has a bulk porosity of up to 54%.[43] A continuous growth of porosity occurs in the multistage reduction of ferric oxide to the metal, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow \rightarrow FeO \rightarrow Fe$, in the dissociation of oxides, sulphides, oxalates, and carbonates, and also in the dehydration of hydrates. In this connection the studies of the overall and differential porosity, the size of the primary crystals, and the total surface areas of the solid phases merit attention[15,44–48].

In concrete cases various mechanisms of the formation of pores obtain. For example, the formation of metal nuclei and submicroscopic pores in oxides or oxide nuclei and pores in carbonates can be represented in two different ways: (a) an unstable transition structure is formed in the bulk of the parent phase; the formation in the latter of a three-dimensional hetero-phase fluctuation, which already has different lattice parameters and smaller distances between its constituent species, should result in its separation from the parent medium, if not over the entire surface then at least partially (Fig. 2*a*); (b) when a nucleus forms on the surface of the initial phase due to an orientation effect (epitaxy), it draws its "constructional material" from the surrounding medium. The loss of mass in the immediate vicinity of the nucleus should initiate the formation of a pore (Fig. 2*b*).

It is important to note that in both cases, regardless of mechanism, the appearance of the nucleus of the new phase is accompanied by the formation of two new interfaces: between the initial solid phase and the new solid phase and between the new solid phase and the gas. This may be accompanied by the regeneration of the interface between the initial solid phase and the gas. This factor along requires the correction of Eqn. (12), as was done in our earlier review by the present author[35].

A mechanism for the formation of pores in the dehydration of hydrates was proposed by Garner[49] (Fig. 2*c*). Wagner[50] put forward a mechanism for the development of a pore in the reduction of wustite (Fig. 2*d*). The primary defect of this mechanism is that it accounts only for the development but not the formation of the pore. It is quite clear that in the reduction of wustite to iron pores not only develop but new ones are actually formed.

Pores are not necessarily formed only when the volume of the new phase is smaller than that of the initial phase but also when the opposite relation between phase volumes holds. For example, in the conversion of copper, nickel, and iron wires into the corresponding oxides, sulphides, and selenides the cations move faster than anions. As a result, there is, as it were, a dispersal of the mass of the metal from the surface towards the periphery; pores are formed which can coagulate and give rise in the limit to a cavity with the same geometrical shape and dimensions as the initial specimen[51].

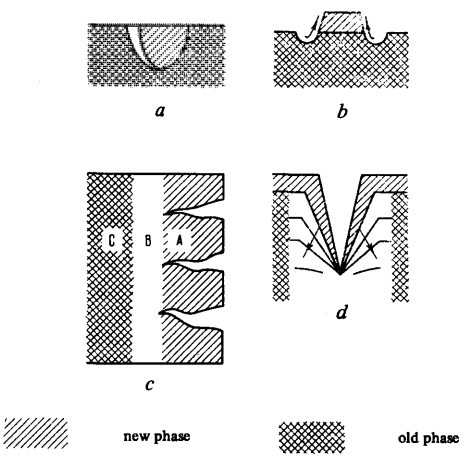

Figure 2. Mechanisms of the formation and growth of pores in topochemical processes:
a) the formation of a nucleus and pore within the parent phase[61]; *b*) the formation of the nucleus of the new phase on the surface of the old; *c*) the formation and growth of pores in the dehydration of hydrates[49] [*A*) new phase; *B*) transition layer; *C*) old phase]; *d*) the development of the pore in the reduction of wustite[50].

The formation of pores renews or maintains contact between the gaseous and solid reactants[42,52], shortens the diffusion path[42], and sets up the conditions necessary for the penetration of electric fields into the bulk of the crystal, which gives rise to the possibility, for example, of the reduction of oxides to metals at temperatures so low that the reoxidation of the latter cannot take place to a significant extent[53].

The experimental data on pore formation throw doubt on the exceptional role which has been attributed to the A–B interface in the development of autocatalysis. A typical autocatalytic reaction is the thermal decomposition of oxalates. For example, Jacobs and Kureishy[14] obtained S-shaped kinetic curves for nickel oxalate both in the powder and compressed states.

Let us consider the dissociation of oxalates:

$$Ag_2C_2O_4(\text{solid}) \rightarrow 2Ag(\text{solid}) + 2CO_2(\text{gas}), \quad (14)$$

$$PbC_2O_4(\text{solid}) \rightarrow Pb(\text{solid}) + 2CO_2(\text{gas}), \quad (15)$$

$$MgC_2O_4(\text{solid}) \rightarrow Mg(\text{solid}) + 2CO_2(\text{gas}). \quad (16)$$

It follows from the ratio of the densities of MnC_2O_4 and M that reactions (14)–(16) should be accompanied by considerable pore formation in the solid product. If one neglects the sintering effect, it is possible to calculate that the porosity of the product formed in reaction (15), for example, may reach about 67% and that of the product formed in reaction (17) may be up to 70%.

Clearly in this case the fundamental decomposition steps on the oxalate–metal surface are hindered. There is no space available for carbon dioxide molecules to desorb into and they cannot dissolve in the atomic lattice of the metal and diffuse through the latter. On the other hand, at the oxalate–gas boundary the reaction is facilitated by the fact that the carbon dioxide molecules can pass freely into the gas phase. Here the decomposition is accompanied by the regeneration of the solid phase–gas interface, breakdown of the crystal, and self-dispersion[13,35].

It is not fortuitous therefore that in recent years investigators have studied the kinetics of thermal decomposition reactions in conjunction with measurements on the changes in the total surface of the solid phase and the porosity occurring in the course of the process. This is evident in the work of Dollimore[15], Gordeeva and coworkers[47], Danes[48], and the present author and Bystrova[43].

The fundamental chemical step in the dissociation of the carbonate, $MCO_3 \rightarrow MO + CO_2$, is the breakdown of the complex anion CO_3^{2-} into a CO_2 molecule and the monatomic anion O^{2-}. It is not difficult to show that this step too is incomparably easier on the carbonate–gas interface than on the carbonate–oxide interface. On the crystal surface, carbon dioxide molecules can be desorbed freely into the gas phase. Their evolution from the outer layers gives rise to vacancies in the anionic sublattice, as a result of which favourable conditions are created for the diffusion of carbon dioxide from the following layers of the crystal lattice. The rearrangement of the crystal lattice of the carbonate into that of the oxide and the formation of a three-dimensional nucleus of the new phase are in no way restricted. On the other hand, on the carbonate–oxide surface the desorption of carbon dioxide molecules is difficult. Their mobility is limited by forces associated with orientation correspondence. The diffusion of carbon dioxide through the calcium oxide lattice involves considerable difficulties. Gel'd et al.[54] showed that calcium carbonate and calcium oxide are virtually immiscible. The diffusion of carbon dioxide on the calcium carbonate–calcium oxide interface also appears unlikely, in the first place because such a surface may not actually exist and in the second place because the forces associated with orientation correspondence must give rise on this surface to a structure almost as compact as that in the bulk of the crystal.

Self-diffusion of carbon dioxide in the calcite lattice is impossible. This was demonstrated by Haul and Stein[55] by the radioactive tracer method. However, the development of the process due to the evolution of carbon dioxide from the bulk of the crystal or on the calcium carbonate–calcium oxide interface, which is associated with diffusion-dependent inhibition, could not give rise to the high rates of reaction which are observed in practice. Thus the complete dissociation of a small cube of polycrystalline calcite with an approx. 10 mm edge at 1140°C requires only 6–7 min.[43] These studies permit the conclusion that both the rapid development of the process and its acceleration are due in this case to the establishment of conditions of uninhibited (or almost uninhibited) evolution of carbon dioxide, i.e. the continuous regeneration of the "initial solid phase–gas" interface.

Under certain thermodynamic conditions and when the mobility of the particles is sufficiently high, a similar mechanism can also be postulated for the dissociation of oxides, sulphides, and other compounds. Of course, the

fundamental steps will be different. For example, in the dissociation of an oxide the fundamental chemical interaction consists in the removal of an electron (or electrons) from the oxygen to the metal. The subsequent stages involving the formation of O_2 and desorption of oxygen should take place more readily on the surface of the crystal, where favourable conditions for the initiation of the new phase do in fact arise. Consequently, the acceleration of the process can be accounted for no less successfully by the occurrence of the reaction on the crystal–gas interface, the "corrosion" of the crystal, and the development of this interface, and also by an increase in the number of defect sites [13,35].

It is noteworthy that in certain studies on the dissociation of carbonates the "degree of conversion–time" curve was not found to be S-shaped. This was observed in experiments with magnesium carbonate by Gordeeva et al. [47] and in experiments with lead carbonate by Kadlets and Dubinin [56]. In the "Proceedings of the Fifth International Symposium (Munich)" Wanmaker reported a similar conclusion concerning strontium carbonate [15].

In this connection it must be noted that these investigators worked with finely dispersed powdered salts. In Wanmaker's study [15] a relation between the rate of reaction and the dimensions of the particles was observed and the absence of an induction period was explained by the rapid generation of the nuclei of the new phase. One should also bear in mind that the increase in size of the particles, the recrystallisation of the initial preparation, can give rise to a considerable increase of the induction period and change the nature of the kinetic curve.

Thus the classical hypotheses concerning autocatalysis, which attribute exceptional importance to the A–B surface in this phenomenon, unduly reduce the role of the gas phase in the development process and also the role of the contact between the solid phase and the gas. Analysis of the literature data [11–27] shows that the phenomenon of autocatalysis is shown most clearly in interactions between solid and gas where the volume of the new solid phase is less than the volume of the substance consumed in its formation. The product must be fairly porous, so that diffusion-dependent inhibition can be excluded, if only in the initial phase, since the ascending branch of the autocatalytic curve corresponds to conditions determined by the reaction kinetics. The present author believes that the formal extension of the classical hypotheses concerning the mechanism of autocatalysis to the interaction of powders with a gas is therefore particularly inadmissible, and yet this is still encountered in modern literature.

We shall now consider the reduction of oxides to metallic iron, the process most frequently encountered in industry. In most practical cases a number of zones are observed in the reduction of crystalline oxides to the metals. Thus the reduction of fused magnetite, carried out by the present author together with Bystrova, leads to the appearance of metal and oxide zones which are clearly distinguishable even with the naked eye [52]. Under the microscope a transition zone, magnetite grains bordered by iron, is observed. The higher the degree of reduction the narrower is the transition zone and the clearer the boundary between the metal and the oxide. The occurrence of zones in the reduction of higher iron oxides has been observed in numerous studies (see, for example, Refs. 42, 57, 58).

When the oxide is finely ground, the process consists of several stages, the lowest oxide not being reduced until the reduction of the higher oxide is complete. Under certain thermodynamic conditions, the reduction of ferric oxide Fe_2O_3 is characterised by the presence of three stages in the reaction:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe\ . \qquad (17)$$

The phenomenon of a number of stages is difficult to achieve and therefore it has been little investigated. It has been observed, for example, in the work of Rostovtsev et al. [59], who explain the presence of several stages by the synchronisation of the reaction in all the grains of the specimen or the sample, and the phenomenon of autocatalysis observed at the same time is accounted for by the classical mechanism, according to which a reaction an interface develops within each grain. Of course, on the basis of this mechanism it appears logical to assume the synchronisation of the reaction in all the grains of the ore. Otherwise the superposition of the maximum rate in one grain onto the minimum rate in another can lead to cancellation of effects. However, this interpretation of the process mechanism gives rise to the following objections.

1. In the first place the applicability of the classical mechanism of the reaction under the conditions of the experiments actually performed has not been demonstrated.

2. In an atmosphere of pure reducing agents, used in the experiments of Rostovtsev et al. [59], only one phase (the metal) can be stable. Therefore, under kinetic conditions (in the absence of diffusion-dependent inhibition), there could not be several stages.

3. In the synchronous reduction of grains in the absence of retardation of the supply of the reducing gas the duration of the process should be a small fraction of the duration actually observed. Furthermore, it would depend only on the size of the grains and not on the weight of the specimen.

In a conductimetric study of the oxidation and subsequent reduction of thin copper and iron wires it was shown that the time required for the complete reduction is smaller by a factor of tens and hundreds than the total oxidation time [60,61]. The reduction of oxidised iron and copper wires 0.20–0.50 mm in diameter in a stream of hydrogen at 500–900°C requires times ranging from 30 s to several minutes. In Rostovtsev's study the reduction of a finely ground hematite powder, the grain dimensions of which were smaller than the diameter of the oxidised wires in the work of the present author and Ermakov [61], took tens of minutes and sometimes actually exceeded 1 h.

Comparison of these kinetic characteristics throws doubt on the synchronous mechanism of the reaction in all the grains of the specimen. In this connection it appears that the classical explanation of the occurrence of maxima and minima on kinetic curves cannot be universal. One should also remember that in the discussion of the mechanism of autocatalysis in modern literature the concept of the A–B interface, its structural model, are not considered in a sufficiently concrete form. The surface of a pressed oxide powder accessible to reaction with the reducing gas may prove to be extremely large. Thus for spherical particles 0.01 mm in diameter, the total surface per cm^3 of such a powder is about 300 cm^2. [62]

If account is also taken of the presence of defects in the crystal structure of the powder grains and the possibility of the regeneration of this structure and the "oxide–gas" interface during the reduction process, as described above, it becomes clear that, under the conditions of Rostovtsev's experiments [59], the principal site where the reaction takes place may be not the "oxide–metal" interface but the "oxide–gas" interface. However, such a hypothesis requires the revision of the mechanism of autocatalysis and the mechanism responsible for the presence of several stages in Rostovtsev's experiments [59].

In the absence of diffusion-dependent inhibition in the crystal lattice of the solid phase, which is probably the case in the reduction of fine powders, it is essential to take into account in the kinetic analysis of the process the ratio of the rate of penetration of the reducing gas (V_1) through the external geometrical surface of the specimen into its deeper zones (towards the reaction surface) and the rate of the adsorption-chemical step (V_2). The rate V_1 depends on the difference between the concentrations of hydrogen in the centre of the gas stream and within the specimen, and is a maximum at the initial instant of reduction. The second rate (V_2) is associated with the area of the reaction surface and the degree of chemical supersaturation; at the beginning of the process it can be a minimum or even zero.

The penetration of the reducing gas into the specimen and the reverse diffusion of the product gas show to some extent the features of Knudsen molecular flow. Some hydrogen molecules encounter the reaction surface of the oxide comparatively rapidly, while others fail to react and pass into the bulk of the specimen.

According to Roginskii's theory, chemical supersaturation in the system is necessary for the process to occur at a finite rate. Under the conditions of the experiments analysed, it cannot be achieved instantaneously over the entire surface of the solid phase, i.e. throughout the bulk of the specimen. As the process develops, oxidising and inert gases are flushed out of the specimen by the hydrogen and the rate of consumption of the reducing gas increases both due to the increase of the degree of chemical supersaturation and also due to the involvement in the reaction of an increasing number of new sections of the oxide surface.

It appears that in this case it is more correct to attribute the rate of reduction corresponding to the ascending branch of the catalytic curve to the increase in the area of the "oxide–gas" interface and not of the "metal–oxide" interface. On the other hand, as the specimen is "saturated" by hydrogen, the rate of "diffusion" of this reducing gas decreases. Thus the values of V_1 and V_2 approach one another. Therefore the process is initially of the purely kinetic type but after a certain time it becomes of a mixed or even diffusion-dependent type.

In this connection, the phenomenon of several stages can be accounted for by the transition of the process from kinetic to diffusion-dependent conditions. In fact, if the rate of diffusion did not limit the rate of the further development of the process, chemical supersaturation could be fairly rapidly attained not only with respect to the first but also the second and third stages of the reduction. However, then we could not have several stages in the process. The ultimate result of the approach of the rate of the adsorption-chemical step to the rate of supply of the reducing gas is that the chemical reaction maintains in the specimen a gas composition which is close to the equilibrium composition for the given stage. If for some reason the rate of supply of the reducing gas increases, there is also an increase in the degree of chemical supersaturation in the system and hence in the rate of reaction.

The process could be self-regulated. However, the gradual disappearance of the initial oxide phase leads to a decrease in the area of the reaction surface and a lowering of the overall rate of the process, and the ultimate result is that the rate of penetration of the reducing gas again begins to prevail over the rate of its consumption in the given reaction stage: supersaturation with respect to the next stage is established.

In this way it is possible to explain the mechanism of autocatalysis and the phenomenon of several stages in the reduction of powdered oxides without resorting to the concept of the "metal–oxide" interface as the reaction surface, the doubtful hypothesis of the synchronisation of the reaction in all the specimen grains being eliminated. This mechanism is in good agreement with theory and experiment. A mathematical interpretation would be desirable for its further justification[63].

The above analysis of the conditions of autocatalysis and the stepwise reaction phenomenon in the reduction of higher oxides shows that an explanation, other than that given in the literature, of the minima and maxima on the kinetic curves for the relevant processes is possible. The formation of the A–B interface cannot by itself accelerate the process. It is also necessary to eliminate the inhibition of the transport of the reactants, i.e. to ensure that they come into contact. In many cases the successful occurrence of the process is probably associated with sufficiently high mobility of the fundamental species. In the low-temperature oxidation of metals the formation of very thin passive films several ångströms thick, which separate the reactants in space, leads to almost complete cessation of the process. If in this case autocatalysis does in fact take place, it is quite clear that the maximum rate is achieved on attaining a degree of reaction which is difficult to determine quantitatively even by the most refined experimental methods.

On the other hand, when the mobility of the species and the porosity of the product are sufficiently high and satisfactory contact is achieved between the reactants, the maximum rate can be attained at high degrees of reaction, which are readily determined experimentally. For example, in the reduction of cuprous and cupric oxides with carbon monoxide the highest rate was observed at high degrees of reaction, amounting to 20–70%, depending on the experimental conditions[64].

All that has been said does not exclude a certain role of the A–B interface and of the product B and its physical state in the kinetics of the reaction.

III. CATALYSIS BY A SOLID PRODUCT

In recent years the problem of catalysis by a solid product has been discussed frequently. Some authors believe that catalysis by a solid product is a specific feature of topochemical processes[25,32,65–70], while others deny that the product has any effect on the rate of reaction[30,31,56,71–74]. Each investigator bases his view on particular experimental data. In all the above investigations the area of the reaction surface could not be estimated. This is not only because of the difficulty of an accurate determination of the surface area of solids. It should be borne in mind that in powdered preparations the true surface area, which may be very high, in some cases cannot be entirely involved in the reaction at once and in crystalline specimens the area of the reaction surface changes during the process due to the "corrosion" of the crystals.

The present author believes that a categorical formulation of the question of the inevitable catalytic effect of the solid product on the topochemical reaction, in isolation from the experimental conditions and the physical state of the solid phases, is pointless. This follows if only from the vast experimental data which show that the appearance of the product can both accelerate the process (catalysis) and retard it (impedance). Therefore the assertion by Sakovich and Boldyrev[32] that the solid product formed in the reaction must *always* (author's italics) have a catalytic effect on the further process when there is an interface

between it and the initial material can be scarcely regarded as valid.

We shall now consider certain examples. In their study of the decomposition of silver oxide, Pavlyuchenko and Gurevich determined the rate of reaction from the change in the pressure of the oxygen evolved per unit time[31]. They observed that, when silver oxide was mixed with powdered silver obtained by the decomposition of the oxide, the rate of reaction did not change. However, complete removal of the product by careful treatment of the partially decomposed silver oxide with mercury did not retard but actually accelerated the process. Probably in this case catalysis by the product could not occur, being suppressed by the blocking effect of the silver produced. It is known that in some cases at high degrees of chemical supersaturation the reaction MO → M leads to the appearance of a very thin layer of metal which separates the initial phase from the gaseous medium and inhibits the process[50,75-77]. Earlier it was observed[70] that the mercury additive does not affect the rate of decomposition of AgO, the presence of copper has no effect on the decomposition of CuO[73], etc.

However, one cannot compare the effect of a product mixed mechanically with the initial preparation, and therefore making a very imperfect contact with the former, with the effect of a product formed as a result of the reaction, and as a rule corresponding to the parent phase as regards orientation and dimensions[78]. According to certain investigators, the catalytic effect of the product can occur only in those cases where there is sufficiently satisfactory contact between it and the initial substance. For catalysis, it is necessary to have a distinct interface between the solid phases. Boldyrev[25,79] frequently drew attention to this condition.

Boldyrev investigated together with Ermolaev the catalytic effect of solid products in the reduction of nickel and copper oxides with hydrogen[25]. The dimensions of the NiO and CuO particles were in the range 0.01–0.06 mm. It was found that, if NiO is subjected to partial preliminary reduction with hydrogen, the rate of its subsequent reduction under the same conditions is very much higher than the rate of reduction of the initial oxide. On treatment of the partially reduced NiO with a solution of mercuric nitrate, the rate-of-reduction curve was almost identical with the curve for the pure oxide. According to the authors, this proves the catalytic effect of the product.

Possibly this is so. However, can one regard such proof as unambiguous? Probably not. Above, the present author showed that the "corrosion" of crystals during the process and the reproduction of the initial solid phase–gas interface, the porosity, and also the defects in the crystal lattice can greatly accelerate the reaction. It is noteworthy that in the experiments of Boldyrev and Ermolaev the effect of these factors was not excluded. The "washing out" of the reaction centres and microcrystals by treatment of the partially reduced oxides with a mercuric nitrate solution can give rise to capillary forces so high that the defects are undoubtedly "healed", i.e. the initial preparation is "aged". This last condition must always be taken into account in the analysis of the kinetics of topochemical reactions[5]. Consequently the retardation of the process can be caused not only by the removal of the product (the catalyst) but also by other factors.

From the above standpoints, one can scarcely regard the catalytic effect of the product in experiments on the decomposition of pyrite as unambiguously proved[80]. Here there is a break in the kinetic curve, beyond which the rate of dissociation increases sharply. X-Ray diffraction studies confirm that, before the appearance of the break, a solid solution was formed, while beyond it crystals of the product were deposited. However, it remains obscure whether the acceleration of the process is due to the catalytic effect of the product or due to autocatalysis caused by an increase in the area of the reaction surface.

The essential feature of the mechanism of the accelerating effect of the product on the topochemical reaction is that the step involving the addition of a fundamental particle to an already existing small crystal of the new phase requires a smaller expenditure of energy (per gramme atom or per particle) than the formation of the three-dimensional nucleus of the new phase itself. In other words the activation energy for the two-dimensional growth of the new phase must be smaller than the analogous quantity for the three-dimensional growth of the solid product. Even a small difference between the two activation energies can give rise to an appreciable difference between the rate constants for the three-dimensional (k_V) and two-dimensional (k_S) growth of the new phase, since both k_i and E_i are related by the exponential expression

$$k_i = k_i^0 e^{-\frac{E_i}{RT}} . \qquad (18)$$

These postulates constitute the basis of the explanation of a number of features of the mechanism of topochemical reactions, for example in the work of Esin and Gel'd[37], Boldyrev[11], and others. Thus the following microscopic picture of the mechanism for the thermal decomposition of an oxide is suggested[21,81]. On the metal–oxide interface, electrons pass from the O^{2-} anion to the metal. As a result of the "relay" transition of electrons, an oxygen ion and not an oxygen atom will appear in the neighbourhood of the metal. An oxygen atom will appear on the outer surface of the oxide in the neighbourhood of the gas phase. The accumulation of such atoms should result in the formation of molecular oxygen and its desorption. A negatively charged crystal of a metal grows by attracting cations from the oxide lattice.

Apart from definite advantages, the mechanism has certain disadvantages. It is invoked in order to explain the catalytic effect of the product and therefore it is based on the presence of a distinct interface between the oxide and the metal. The growth of the metallic phase at this interface without the removal of oxygen anions should involve considerable steric hindrance. But the mechanism does not explain where and how the oxygen anions are removed.

The diffusion of oxygen, which is a slow process, could complicate the reaction. On the other hand, the occurrence of the process under kinetic conditions is evidence of unhindered removal of oxygen. This can be explained on the basis of the difference between the volumes of the new and old phases, leading to continuous regeneration of the pores, the oxide–gas interface, and the defects in the surface layer of the oxide. Probably this mechanism, taking into account the formation of pores and defects, may prove quite acceptable also for the reduction of oxides to metals by gaseous reducing agents.

Turning again to the relative values of the activation energies for the growth of the new phases in the bulk (E_V) and on the surface (E_S), it must be emphasised that in principle one cannot exclude also the possibility that

$$E_S > E_V \qquad (19)$$

In a slightly different form this confirms the principle of correspondence as regards orientation and dimensions, formulated on the basis of the systematic examination of the experimental data: "the phase reaction on the surface of a solid involves the formation of a new crystal lattice which corresponds, as regards orientation and dimensions,

to the crystal lattice of the initial surface if the energy (E) of deformation of the two-dimensional lattice of the new phase is smaller than the work (A) required for the formation of its three-dimensional nucleus... Otherwise, when $E > A$, the process takes place independently of the structure of the surface of the initial phase"[82]. Here it is appropriate to recall yet again Erofeev's data[17] on the formation of an amorphous product on the A–B interface. The above scheme probably does not exhaust the possible different versions of the mechanism of process catalysis by a solid product.

The accelerating effect of the gaseous product in some cases is striking. Thus the thermal decomposition of potassium azides takes place more rapidly in the presence of potassium vapour than in a vacuum[83]. The experimental data obtained by Tumarev and Pushkarev[84], who investigated the reduction of powdered cupric oxide (–0.050) [particle size 0.050 mm? (Ed. of Translation)] and a gaseous reducing agent (carbon monoxide) are of considerable interest. The product obtained was used as an activator. Three types of experiments were tried: (1) a 0.5 g layer of the activator was placed under a CuO sample (4 g), (2) 0.5 g was mixed with the sample, and (3) a 0.5 g layer was placed on top of the sample. In all cases the presence of the activator resulted in the reduction of cupric oxide at temperatures below 100°C, i.e. under conditions where the process did not develop in the absence of the product. The activator placed underneath the oxide sample proved to have the greatest effect, while the layer of activator on top of the sample to be reduced had no catalytic influence. The authors concluded that the catalysis is due to the activation of the reducing gas by the solid product. They postulate the desorption of the gas from the surface of the catalyst, which retains its activity during a period sufficient for transition to the reaction zone. It would be interesting to test how a change in the distance between the activator and the sample being reduced affects the interaction. Mass-spectrometric (or some other) analysis of the gas which has just passed through the layer of activator would be valuable.

The present author believes that in this case we are dealing with an unusual version of a chain reaction mechanism: an increase in the amount of the solid product results in an increase of the number of activated species in the gas phase which in turn accelerates the conversion of the initial solid phase into the product. Of course under these conditions the area of the reaction surface and its regeneration must be such that unhindered utilisation of an increasing amount of activated species from the gas phase is permitted. The attainment of a maximum rate and the subsequent retardation of the process must be treated here as a stage in which the capacity of the oxide surface to utilise all the active species from the gas has been exhausted.

Tumarev and Pushkarev's experiments confirm the present author's view, stated earlier, on the role of the gas phase, the porosity, and the oxide–gas interface in the mechanism of the reduction of oxides to the metals by gaseous reducing agents[35,61,63]. At the same time, Boldyrev's assertion[79] that the catalytic effects of the product can be shown only when the contact between the latter and the starting material is sufficiently good, probably cannot apply to all cases of acceleration of topochemical processes by the new solid phase.

When autocatalysis in the reduction of oxides to the metals is approached from the standpoint of electronic hypotheses, it is noteworthy that the formation of the metallic phase may be accompanied by a sharp increase in the number of free electron-acceptor energy levels. This in turn may facilitate and accelerate the reducing gas chemisorption stage, and may increase the amount of adsorbate on the surface of an oxide with mixed (electronic-ionic) conductivity[8,12,15]. Here the assertion[79] that contact between the solid phases is essential for catalysis to take place appears to be quite appropriate.

Analysis of the possible reasons for the acceleration of reactions (1) and (2) shows that they may be different, for example, in the dissociation of oxalates and carbonates, on the one hand, and the reduction of oxides, on the other. While in the first case the breakdown of the crystals, self-dispersion and regeneration of defects, can have a decisive effect on the course of self-acceleration, in the second case one must take into account the electronic factor in the chemisorption of the reducing gas. Thus analysis of the literature data leads to the following conclusions.

1. The classical mechanism of autocatalysis, which is based on the increase of the area of the interface in the course of the process is inadequate and cannot be universal.

2. Autocatalysis due to the increase in the area of the reaction surface and catalysis by a solid product are so mutually interconnected that in most experiments it is difficult to separate them and to investigate them in a pure form.

3. The gas phase, the development of porosity, and the regeneration of contacts between the initial solid phase and the gas play a major role in the development of autocatalysis.

4. Catalysis by the product can occur only when its inhibiting effect on the process is suppressed.

In connection with this last feature of the topochemical reactions analysed, the impedance phenomenon will be examined in greater detail.

IV. THE IMPEDANCE PHENOMENON

Numerous experimental data have now accumulated, showing how the physical state of the product influences the kinetics of the relevant topochemical reactions. It has been observed that in some cases the formation of the product lowers the rate of reaction. This is explained by the blocking of the initial solid phase, the separation of the reactants, and the occurrence of diffusion-dependent retardation. In other cases the product does not prevent appreciably contact between the reactants and cannot significantly retard or stop the process.

The available experimental data will now be quoted and initially those cases will be considered where the formation of a product separates the reactants and sharply reduces the rate of reaction.

1. All metals, except the noble metals, are thermodynamically unstable under the usual atmospheric conditions and should be oxidised. However, most of them, except for the alkali and alkaline earth metals, virtually do not oxidise. It has been shown that the reason for this stability is the formation of a thin protecting film of oxide, which separates the reactants and prevents further interaction of the metal with atmospheric oxygen[85].

2. High-temperature oxidation of metals yields in many cases a dense layer of scale, which lowers the rate of the process. The direct interaction between the oxidising gas and the metal is replaced by a slow diffusion-dependent process.

3. The blocking of the initial phase has proved to be particularly successful when the system is alloyed to

impart to it heat-resistant properties. Arkharov showed[86] that in this case high-temperature oxidation leads to the formation of a dense protective layer, consisting of spinel-type oxides with the smallest possible lattice constants.

4. Isothermal carbonation of calcium oxide crystals takes place with great difficulty, since the product (calcite) has a smaller density than the initial preparation and a continuous coating is formed. One may refer to the example quoted by Rostovtsev[87]: lime obtained by the heat treatment of calcite required exposure for three days to an atmosphere of carbon dioxide at 850°C in order to reabsorb two thirds of the carbon dioxide evolved.

5. In experiments on the reduction of polycrystalline specimens of fused magnetite with hydrogen the process was found to be retarded from its very beginning[52]. Despite its porosity, the coating produced presents a definite obstacle to the penetration of the reducing gas into the reaction zone. In this case Knudsen molecular diffusion of the gases (the reactant and the product) occurs. However, even such migration of gases can prove to be the rate-limiting step of the process.

6. In the reduction of natural magnetite single crystals Edstrom observed considerable inhibition of the process due to the formation of a compact layer of wustite as the product[42].

7. The reduction of oxides sometimes leads to the formation of the metal as a thin compact layer, although the appearance of a porous product would be expected from the relative volumes of M and MO. Thus in the reduction of cuprous oxide with carbon monoxide vigorous formation of metallic copper is observed from the very beginning of the process, so that, over a very short period, the initial solid phase becomes covered by a compact copper film, which protects the entire specimens from further action of carbon monoxide; the reduction of Cu_2O ceases[75].

A similar phenomenon was observed in the reduction of wustite with hydrogen[50,76]. Electron-optical studies showed that the iron film formed did not have any pores. In this case the reaction is very slow. According to the authors it was possible only by virture of the diffusion of oxygen through the thin metal film. Calculation of the activation energy for such diffusion gives 53 000 ± 4000 cal g-atom O.

8. The sintering or recrystallisation of spongy metal in the reduction can retard the reaction. This was observed, for example, in the experiments of Chufarov and Lokhvitskaya[22] in the reduction of magnetite with hydrogen and also in a comparative conductimetric study of the rates of oxidation of copper and the reduction of its oxides[60].

Here one should also bear in mind the possibility of a lowering of the catalytic effect of the product with increase in temperature. For example, the iron catalyst for the synthesis of ammonia is prepared by the fusion of iron oxides with K_2O, CaO, Al_2O_3, and SiO_2 additives with subsequent reduction of this mixture of oxides with hydrogen to the attainment of an active state[88]. As the reduction temperature is raised, the catalyst surface is deactivated.

At any rate the experimentally observed negative temperature coefficients of the rates of the topochemical reactions analysed probably cannot be attributed solely to the sintering and recrystallisation of the product.

9. It should also be noted that any autocatalytic process is completed with a continuous decrease of rate, which corresponds to the descending branch of the "rate–time" kinetic curve. The retardation of the process is not due only to the narrowing of the reaction front but also to an increase in the thickness of the outer layer of product[89]. In many cases one can observe how autocatalysis is replaced by impedance.

The above examples have been quoted to illustrate the role of impedance in the kinetics of reactions of types (1) and (2).

V. UNBLOCKING OF THE INITIAL SOLID PHASE

The weakening of the impedance or its suppression play an important role in the kinetics of the processes analysed. We shall now examine the experimental data which show that the loosening of the product and also the improvement of the contact between the reactants facilitate the process and accelerate it. Here the following data are relevant.

1. When the oxide film protecting the metal from the effect of the gas phase is scratched, the contact between the reactants is restored. This phenomenon is used to dissolve the metal and to isolate the protective film in a "pure" form, which constitutes one of the experimental proofs of the existence of protective films[29].

2. Periodic cracking of the scale under the influence of stresses arising in it during the high-temperature oxidation of metals is reflected in breaks on the kinetic curve. The breaks can be explained by the acceleration of the process due to the renewal of contact between the metal and the gas phase each time the scale cracks[90,91].

3. The oxidation of alkali and alkaline earth metals is accompanied by the formation of a loose layer of products. Even at room temperature under the usual atmospheric conditions the initial solid phase is completely converted into oxide after a relatively short time. Here one may refer to numerous experimental data: a typical example is the oxidation of barium at 17°C in "room" atmosphere[92].

4. In 1941 Arkharov established that the rate of oxidation of iron increases with the appearance of a wustite layer in the scale[93]. The appearance of structures with cationic vacancies (wustite or the porous modification of hematite) facilitates the diffusion of iron ions and accelerates the oxidation process. The heat resistance principle formulated by Arkharov is based on the prevention of the formation of the wustite phase and the creation of conditions for the formation of dense oxides of the spinel type[86].

5. Carbonate dissociation processes take place much more rapidly than the reverse reactions. The thermogram for the dissociation of calcium carbonate and the carbonation of calcium oxide, recorded by Potapenko for the same specimen[94], is very instructive in this respect. Heating and cooling of the preparation in a stream of carbon dioxide results in two temperature arrests, at about 918° and 888°C, the extent of the first being much greater than that of the second. Consequently at a given rate of supply or removal of heat, the amount of carbonate decomposed is greater than the amount formed. This is the result of the different rates of diffusion of carbon dioxide through the coating, which proves to be looser during dissociation (calcium oxide) than during carbonation (calcium carbonate).

6. In the reduction of oxides and ores to the metals the reaction product is frequently porous with an extremely large surface area. The methods of preparation of pyrophoric metals by reducing polycrystalline specimens at low temperatures are widely known. The reduction of iron ore usually results in the formation of "spongy" iron.

Bogdandy et al.[46], who investigated the mechanism of the reduction of porous iron ore, concluded that in most cases contact between wustite and the reducing gas is not impaired by a layer of metallic iron. On the basis of microscopic studies, Edstrom[42] explained the faster reduction of ferric oxide compared with other iron oxides by the earlier and more abundant formation of pores in the products.

7. A comparative conductimetric study[61,95] of the rates of oxidation and reduction of iron revealed marked loosening of the metal after the completion of the cycle incorporating the forward and reverse reactions. Because of this, the time consumed in the reduction of wire specimens until the recovery of the initial resistivity proved to be much lower than in the oxidation. Sometimes this difference is as much as 100%.

8. The crystallisation process in the dehydration of hydrates is accompanied by the formation of cracks (pores), usually perpendicular to the interface between the solid phases[96]. These pores facilitate the subsequent development of the process.

9. Some investigators have shown that the removal of the product blocking the initial solid phase and separating the reactants accelerates the process. For example, Pavlyuchenko and Gurevich observed that the removal of the product accelerates the decomposition of silver oxide[31].

Thus numerous experimental data suggest that in reactions between solid and gaseous substances the unblocking of the solid phase blocked by the condensed product may significantly facilitate the process. We now see the great importance of the physical state of the product in the kinetic analysis of reactions (1) and (2). Therefore a systematic arrangement of all these data, i.e. their generalisation in a single rule or principle is extremely desirable. This has been done only in the field of chemical corrosion of metals.

VI. THE PILLING–BEDWORTH RULE AND THE PRINCIPLE OF THE ACCELERATION OR RETARDATION OF REVERSIBLE TOPOCHEMICAL REACTIONS WITH PARTICIPATION OF GASEOUS AND SOLID REACTANTS

In 1923 Pilling and Bedworth[34] formulated a rule for the isothermal oxidation of metals, the significance of which is that the formation of a compact film of oxide on the metal inhibits the subsequent interaction of the latter with the gas, while the appearance of a loose (porous) product does not hinder the process. The type of product formed depends on the relative volumes of the metal oxidised and the oxide produced.

Mathematically the rule formulated by Pilling and Bedworth can be described by two formulae:

$$\frac{V_O}{V_M}=\frac{Md_M}{And_O}<1 \qquad (20)$$

and

$$\frac{V_O}{V_M}=\frac{Md_M}{And_O}>1\,, \qquad (21)$$

where V_O is the volume of the oxide formed in the interaction of one gramme-atom of the metal, V_M the gramme-atomic volume of the metal, A the atomic weight of the metal, M the molecular weight of the oxide, n the number of metal atoms in the oxide molecules, and d_M and d_O are the densities of the metal and the oxide respectively. Eqn. (20) is valid for the oxidation of alkali and alkaline earth metals. Here the formation of a loose film does not lead to the separation in space of the reactants M and O_2:

$$M+\tfrac{1}{2}O_2\rightarrow MO\,. \qquad (22)$$

According to other hypotheses[29], a very thin pseudomorphous film of oxide forms between the solid phases and cannot cause serious diffusion-dependent inhibition of the process. Therefore the law governing the growth of the oxide layer is linear.

Eqn. (21) holds in the oxidation of most of the technically important metals (aluminium, zinc, copper, nickel, manganese, iron, chromium, cobalt, tungsten, etc.). It leads to a parabolic or a logarithmic relation between the weight of the oxidised metal (or the thickness of the oxide film) and time [Eqns. (4) and (5)].

The Pilling–Bedworth rule is of limited applicability for the following reasons:

1. It takes into account only the ratio of the volumes of the solid phases, disregarding their structural features.

2. Apart from the true volume of the oxide, there exists also the apparent volume. The difference between the rates of diffusion of ions in the high-temperature oxidation of metals, for example, results in the apparent volume of the oxide becoming much larger than the volume calculated from the ratio of the densities of M and MO.

The experiments of Wagner[97] and Ol'shanskii[51] on the conversion of silver and copper into their sulphides showed that the process occurs via the preferential diffusion of the cations through the layer of the solid product. This leads to the appearance and coagulation of pores. In the limit cavities may form, which are, as it were, negative imprints of the oxidised specimen.

The formation of iron scale under industrial conditions is accompanied by the appearance in the inner layers of macropores which are visible even with the naked eye.

3. The occurrence of internal stresses in the oxide layer due to the different densities of the metal and the oxide, phase transitions, temperature oscillations (deviations from the specified temperature of the process), and other factors leads to the cracking of the scale, which may result in the degeneration of the parabolic relation to a linear relation, for example, as shown in Fig. 3.

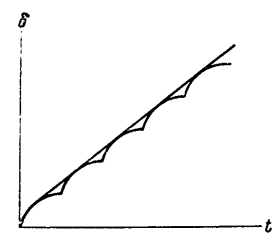

Figure 3. Transformation of a parabolic relation into one of a pseudolinear type.

4. It is possible to select such process conditions that, when Eqn. (21) holds, the product is loose (porous) and, conversely, when the inequality (20) holds, the product may become compact.

The development of the theory of the oxidation of metals suggests that the mechanisms of chemical and electrochemical corrosion have much in common, in addition to certain differences. Thus, according to the data of a number of investigators[51,98,99], chemical oxidation of a metal should be regarded as due to the operation of electrochemical cells in which the role of the metallic conductor and the electrolyte is fulfilled by the oxide phase which exhibits

mixed (electronic and ionic) conductivity. Electrochemical oxidation is also treated as the result of the operation of electrochemical corrosion cells[29].

However, in one case (in chemical oxidation) the reaction between iron and oxygen yields a compact oxide film. As a result, the reactants are separated in space, the process is retarded, and is possible only via the diffusion of elementary species. In another case (in electrochemical corrosion of iron) the product (rust) may be porous despite the fact that its volume is greater than that of the metal oxidised.

5. Finally, it is possible to set up such temperature conditions that the loose oxide begins to sinter, and, despite Eqn. (20), the process is retarded and the linear relation in kinetic plots is converted into one of a parabolic or logarithmic type; on the other hand, on loosening or sublimation of the compact oxide, it is possible to obtain a linear relation between the weight of the metal which has reacted and time.

The above considerations lead to the following conclusion. Under the conditions of isothermal oxidation of the metal, the protective film does not always have the density and the structure of the compact oxide of the same composition. Consequently, the main factors which influence the acceleration or inhibition of the process are not those defined by formulae (20) and (21) but the physical state of the product and the mechanism of the reaction. This conclusion is even more convincing if one goes beyond the limits of chemical corrosion into the wider field of topochemical reactions described by formulae (1) and (2). This is demonstrated by numerous experimental data, described in sections IV and V of the present review and in the literature[9,11,13,15].

Thus one may conclude that the modern state of the theory of topochemical processes analysed in the present article is not yet consistent with the experimental data which have accumulated. The Pilling–Bedworth rule and also Arkharov's heat-resistance principle have played a major role in the determination of the general trends in the acceleration or retardation of topochemical reactions; however, their applicability is restricted to the field of chemical corrosion of metals.

Dankov's principle of orientational and dimensional correspondence applies directly to the mechanism of the reactions considered. Its great theoretical and practical value is generally known. However, it does not determine directly the mode of acceleration or retardation of the relevant reactions.

One must of course bear in mind that no one rule or principle can pretend to be fully universal and cannot embrace all the wide variety of factors which influence the kinetics of topochemical reactions. How wide is the range of these factors, which include all the chemical and physical phenomena accompanying the development of the process, can be assessed if only from the thermal decomposition of solids[5]. At the same time the systematised experimental data on the blocking and unblocking of the initial solid phase in its interaction with the gaseous medium show how great is the role of impedance in the kinetics of topochemical processes. Analysis of the phenomenon of autocatalysis shows that the maximum rate can be attained at high degrees of reaction only when sufficient contact between the reactants is maintained throughout the entire period of self-acceleration and the chemical reaction takes place under kinetic conditions. It becomes clear that there exists in this field a more general kinetic principle, including as a special case the Pilling–Bedworth rule, of recognised value in the field of chemical corrosion of metals but which requires correction on going to the wider field of topochemical reactions.

Analysis of experimental data permits the formulation of the kinetic principle for topochemical reactions with participation of solid and gaseous reactants under isothermal conditions in the form of the following postulates:

1. When reactions of the type

$$A(solid) \rightleftarrows B(solid) + C(gas),$$

$$A(solid) + C(gas) \rightleftarrows B(solid) + D(gas)$$

are thermodynamically possible, the continuous formation of the product is possible only when the phases [i.e. the initial phase (A) and the gaseous phase] are in contact. An increase of the contact surface by dispersing phase A may accelerate the process, reduce its duration, and increase its extent.

2. The blocking of the initial solid phase by the product B (or A in the reverse reaction) leads to the separation in space of the reactants and the occurrence of hindrance to the process, which undergoes a transition from kinetic to diffusion-dependent conditions. Then both the rate of diffusion of elementary species through the crystal lattice of the compact product and the rate of Knudsen molecular flow may prove to be the rate-limiting component of the topochemical reactions considered.

3. When the solid phase is unblocked as a result of the cracking of the layer of product, by the formation in the latter of pores, or by its artificial loosening or even removal (for example by sublimation), the reaction may be significantly facilitated even under diffusion-dependent conditions, and under favourable circumstances (effective unblocking) may result in a return to kinetic conditions. Then, if during some period spontaneous growth of the reaction surface or an accelerating effect of the product is observed, the process may become autocatalytic.

In conclusion it must be emphasised that the above postulates are of the kinetic type and have nothing in common with the thermodynamic principle of the displacement of equilibrium (the Le Châtelier–Braun principle[100]), according to which the removal of the product should favour a higher degree of conversion regardless of the time consumed.

The necessity for a clear formulation of the principle governing the acceleration or retardation of topochemical reactions is dictated by the following considerations. In the first place the kinetic rules and principles available at the present time (the Pilling–Bedworth rule and the Arkharov principle) are restricted to the field of chemical corrosion. However, the experimental data which have accumulated show a considerable influence of the physical state of the product on the kinetics of a wider range of topochemical processes. Secondly the formulation of the principle should indicate the general pathways involved in the acceleration (and, where required, also retardation) of isothermal reactions of the given type. Thirdly one can encounter in the literature directly opposed views: some authors believe that the product inevitably accelerates the process, while others reject this. The above general principle shows that, depending on the process conditions and the physical state of the interacting solid phases, three cases are possible: (1) the product does not influence the rate of the process; (2) the product accelerates the reaction (catalysis); (3) the separation of the reactants by the product inhibits the process (impedance).

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Astatine

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CONTENTS

1. History of discovery 87
2. Isotopes of astatine 88
3. Astatine in nature 89
4. Methods of obtaining and isolating astatine 89
5. Physical properties of astatine 90
6. Chemical properties of astatine 91
7. Astatine in organic compounds 95
8. Biological behaviour of astatine 96

Astatine is the rarest element on our planet. The Earth's crust contains ~70 mg, among the short-lived members of the natural radioactive families[1]. Astatine became available to investigators only after it had been obtained as a result of nuclear synthesis, therefore it is justifiable to classify it among the synthetic elements.

Despite the fact that the chemical properties of astatine began to be studied a quarter of a century ago, much concerning the behaviour of this element is uncertain and at present we know relatively little about it. This is due primarily to the absence of stable and long-lived isotopes of astatine, which makes it inevitable that all investigations be made at the ultramicro-level with all the associated difficulties. Moreover, it must be borne in mind that astatine is capable of forming a large number of valence states, some of which exhibit high reactivity.

By exhibiting non-metallic properties in some instances and metallic in others, astatine is one of the most interesting elements of the Periodic System.

I. HISTORY OF DISCOVERY

Mendeleev first predicted the existence of the 85th element of the Periodic System. At the start of the nineteen-twenties Wagner[2], starting from the physical basis of the Periodic Law, again predicted the existence of a fifth member of the halogen subgroup. At this time intensive searches for it in natural materials began. Reports of the discovery of element 85 appeared one after another[3-7]. Definite chemical properties were ascribed to the newly discovered element and it was given sonorous names: alabamine[6], helvetium[7], anglo-helvetium[8], leptine[9], daccine[10]. A more thorough verification of the separation and methods of identification of element 85, which were used in studies noted earlier, led to the conclusion that its existence was not proved[11-14]. The mass-energy dependence for heavy nuclei[15] shows that in element 85 the proton : neutron ratio is such that considerable stability cannot be expected for the nucleus of the element, and consequently of its isotopes of long half-life also. In natural materials element 85 is encountered solely in trace amounts as a short-lived daughter product in the natural radioactive series. The search for this element in natural materials by use of chemical methods of separation developed for its nearest analogue, iodine, was unsuccessful. Above all this was due to the time consumption of the methods for separation from the natural materials and the absence of sufficiently long-lived isotopes of element 85. Karlik[16] and Hulubie[17] reviewed critically the unsuccessful searches for the missing halogen and the erroneous reports of its discovery.

The first reliable report of the discovery and identification of element 85 appeared in 1940 in a paper by Corson and coworkers[18], who obtained it in the bombardment of a bismuth target by helium ions in the 60-in cyclotron of California University, by the reaction:

$$^{209}\mathrm{Bi}\,(\alpha,\,2n)\,^{211}\mathrm{At}.$$

Subsequently, the discoveries of this element gave it the name astatin[19] from the Greek αστατος (unstable): this name well describes its nature. Until 1960 the name астатин [astatin] was widely used in the Russian chemical literature but the name of this element has now been shortened to астат [astat].

2. ISOTOPES OF ASTATINE

Twenty isotopes of astatine are now known. Their main radioactive characteristics and the nuclear reactions by which they were obtained and identified are shown in Table 1.

It must be noted here that almost all the known isotopes of astatine are also formed by reactions of deep fission of thorium and uranium by high-energy protons[21-23].

Fig. 1 shows a plot of the relation between the α-particle energies and the mass numbers (and number of neutrons) of the isotopes of astatine[24]. As Table 1 and Fig. 1 show, the most long-lived isotopes of astatine have a number of neutrons close to 126, which corresponds to the formation of a completed nuclear shell[25,26]. The form of the curve in Fig. 1 shows that the light isotopes should have very short half-lives and disintegrate with the expulsion of high-energy α-particles. Moreover, in possessing a considerable neutron deficiency they will certainly be unstable to the capture of an orbital electron. On passing to the neutron-surplus region ($A - Z = 126$) the curve has a break, which shows a sharp decrease in the strength of the bonding of the nucleons in the nucleus—all the isotopes of astatine with $A > 211$ have very short half-lives. The heaviest isotopes of astatine ($A \geqslant 219$) show some stability towards α-decay. However, in this range transitions by β-decay are also possible[27,28]. Several authors have suggested that astatine, like elements 43 and 61, cannot have β-stable nuclei at all[29].

Figure 1. Energy of the α-particles of the isotopes of astatine plotted against mass number (and number of neutrons).

Table 1. Isotopes of astatine[20].

Isotope	Half-life	Type of decay	Energy of α-particles, MeV	Method of production
^{200}At	0.8 min	α	6.42 (~60%) 6.47 (~40%)	Au + ^{12}C
^{201}At	1.5 min	α	6.348	Au + ^{12}C, ^{14}N, ^{16}O
^{202}At	3 min	α (12%) e.c. (88%)	6.133 (64%) 6.231 (36%)	Au + ^{12}C, ^{14}N, ^{16}O
^{203}At	7.1–7.4 min	α (14%) e.c. (86%)	6.09	Bi (α, 10n) Pt + ^{14}N Au + ^{12}C, ^{14}N, ^{16}O
^{204}At	9–9.3 min	α (4.5%) e.c. (95.5%)	5.95	Bi(α, 9n) Au + ^{12}C, ^{14}N, ^{16}O
^{205}At	22.7–26.2 min	α (18%) e.c. (82%)	5.90	Bi (α, 8n) Au + ^{12}C, ^{14}N, ^{16}O Pt + ^{14}N
^{206}At	22–29.5 min	α (0.9%) e.c. (>99%)	5.7–5.9	Bi (α, 7n) Au + ^{12}C, ^{14}N, ^{16}O
^{207}At	1.8–2 h	α (~10%) e.c. (~90%)	5.75	Bi (α, 6n) Au + ^{14}N daughter ^{207}Rn
^{208}At	1.7 h	α (0.5%) e.c. (99.5%)	5.65	Bi (α, 5n) daughter ^{212}Fr
^{209}At	5.5 h	α (~5%) e.c. (~95%)	5.642	Bi (α, 4n) daughter ^{209}Rn
^{210}At	8.3 h	α (0.17) e.c. (>99%)	5.519 (32%) 5.437 (31%) 5.355 (37%)	Bi (α, 3n) daughter ^{210}Rn
^{211}At	7.2–7.5 h	α (40.9%) e.c. (59.1%)	5.862	Bi (α, 2n) daughter ^{211}Rn
^{212}At	0.22–0.305 s.	α	7.60 (20%) 7.66 (80%)	Bi (α, n)
^{212m}At	0.120 s.	α	7.82 (80%) 7.88 (20%)	Bi (α, n)
^{213}At	≪1 s.	α	9.2	decay product of ^{225}Pa
^{214}At	2×10^{-6} s.	α	8.78	daughter of ^{218}Fr in ^{226}Pa series
^{215}At	short	α	8.04	natural daughter of AcA
^{215}At	10^{-4} s.	α	8.00	daughter of ^{219}Fr in ^{227}Pa series
^{216}At	3×10^{-4} s.	α	7.79	daughter of ^{220}Fr in ^{228}Pa series
^{217}At	0.018 s.	α	7.05	daughter of ^{221}Fr in ^{233}U series
^{218}At	1.5–2.0 s.	α	6.6976 (94%) 6.653 (6%)	natural daughter of RaA
^{219}At	0.9 min	α (97%) β (3%)	6.27	natural daughter of AcK

In some papers devoted to the study of astatine isotopes it was noted that ^{208}At has an isomer with a half-life of 6.3 h.[30] The isomers ^{204m}At (25 min) and ^{206m}At (2.9 h) have also been observed[30]. A more thorough check of the half-lives of ^{208}At, ^{206}At, and ^{204}At from the periodically separated daughter polonium did not show the presence of the long-lived isomers noted above[31]. Probably the information on the existence of the isomers is due to methodological errors.

The chemical properties of astatine are most conveniently studied on its relatively long-lived isotopes with mass numbers 209, 210, and 211. These isotopes are usually obtained by irradiating bismuth with α-particles.

The excitation function of ^{209}Bi(α, 2n)^{211}At has been studied in sufficient detail[32,33]. Its threshold is 21 MeV, and the yield of ^{211}At reaches a maximum at an α-particle energy of 26 MeV. It is important to note that for the production of pure ^{211}At free from other isotopes as impurities the energy of the helium ions should not exceed 29 MeV—the threshold of the (α, 3n) reaction. These conditions must be observed when the activity of the astatine is measured by recording α-particles, since ^{210}At decays

by 99% into the 138-day ^{210}Po, which also emits α-particles. True, the decay of ^{211}At by 59.1% is effected by capture of an orbital electron with the formation of ^{211}Po but the latter has the half-life of only 0.52 s, and almost any act of decay of ^{211}At leads to the loss of an α-particle. The α-particle spectrum of ^{211}At has a very characteristic appearance: a line at 5.862 MeV for the α-particles of ^{211}At itself and a line at 7.43 MeV for the α-particles of ^{211}Po. A guarantee of the purity of a specimen of ^{211}At is the ratio of the intensities of the 5.862 and 7.430 energies, which should be 40/60.

The isotope ^{210}At was first obtained[32] by the reaction ^{209}Bi(α, $3n$)^{210}At. As already noted above, the threshold of this reaction is 29 MeV and the maximum yield occurs at 40 MeV. The isotope ^{210}At disintegrates by only 0.17% with expulsion of α-particles with energies of 5.519 (32%), 5.437 (33%), and 5.355 (37%) MeV. The decay proceeds mainly through the capture of an orbital electron and the scheme of the conversions is rather complex[34].

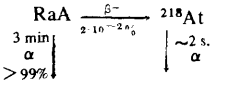
The reaction ^{209}Bi(α, $4n$)^{209}At is most often used for the production of large quantities of the isotope ^{209}At. True, specimens obtained by this method are necessarily contaminated by other isotopes of astatine. A small quantity of completely pure ^{209}At can be isolated as a daughter product from ^{213}Ra, obtained in the irradiation of thorium with protons of energy 350 MeV [21,30].

The isotope ^{209}At decays by capture of an orbital electron and expulsion of α-particles with energy 5.642 ± 0.005 MeV. The α-decay branch totals 5%.[30] Gamma radiation of ^{209}At, which is accompanied by electron capture, consists of four lines.

The principal nuclear properties and the schemes for the γ-transitions for some isotopes of astatine have been reviewed in detail[20].

3. ASTATINE IN NATURE

Starting from the processes of radioactive decay in the uranium series, Hahn[35] predicted the possibility of the formation of isotopes of astatine in the β-decay of polonium[35]. Karlik and Bernert[36], and then Walen[37], observed, in studying the radioactivity of the daughter products of radon, that an insignificant part of RaA (^{218}Po) disintegrates by the scheme:



The presence in a freshly formed specimen of RaA, in addition to α-particles with energy of 5.99 MeV due to the decay of this isotope of polonium, of α-particles with energy 6.63 MeV, served as proof of the formation of ^{218}At in the β-decay of RaA.

The discovery of β-branching in the decay of RaA served as an impetus for studying the polonium fractions of other natural radioactive series with the aim of discovering new natural isotopes of astatine. Karlik and Bernert[38] reported the β-decay of AcA (^{215}Po). They found that AcA undergoes 5×10^{-4}% β-decay, to form ^{215}At, which decays with a period of 10^{-4} s, expelling α-particles with energy 8.4 MeV. Avignon[39] made a more careful investigation and defined the energy of the ^{215}At α-particles (8.00 MeV) and the β^-/α ratio (0.9×10^{-7}) more accurately. This isotope was also observed[40] as the product of the successive α-disintegrations of ^{227}Pa.

On the basis of the regularities in the α- and β-decays in the natural radioactive series it was suggested that as a result of rare instances of α-decay ^{227}Ac forms a little chain parallel to the main series[9]. Hyde and Giorso[41] isolated from the ^{227}Ac source 20 mC francium, in which, ^{219}At was then identified by chemical means. It was shown that ^{219}At has a half-life of 0.9 min, and disintegrates 97% with the expulsion of α-particles with energy 6.27 MeV and 3% undergoes β-decay. This work[41] is the only instance of the chemical identification of an isotope of astatine from a natural source. It has been reliably established that in natural radioactive sources only three short-lived isotopes of astatine, ^{215}At, ^{218}At, and ^{219}At can be detected; these are members of radioactive families. This explains why interest in the search for and investigation of natural astatine has decreased somewhat recently.

4. METHODS OF OBTAINING AND ISOLATING ASTATINE

In the production of astatine in cyclotrons by the (α, xn) reaction a layer of bismuth (50–100 mg cm^{-2}) is applied to an aluminium substrate either as the molten metal or by sputtering. When bismuth oxide is to be irradiated a copper support is employed in the openings of which the Bi_2O_3 is pressed. To avoid loss of astatine at the time of irradiation due to sublimation the back of the support is cooled with water†.

The astatine which is formed as a result of the irradiation of bismuth by α-particles is the main product of the reaction ($\sigma \simeq 10^{-24}$ cm^2) and the contribution of the radioactive isotopes of the other elements is insignificant ($\sigma \simeq 10^{-26}$ cm^2).[42,43] To separate the astatine formed from the main mass of metallic bismuth and from polonium use is frequently made of the high volatility of astatine. The distillation is done in a current of nitrogen (at a few mmHg) or in a vacuum with the target heated to 300–600°C. The astatine vapour is condensed on the surface of a glass trap cooled with liquid air or dry ice. Radiochemically pure astatine is obtained by redistillation[18,44]. The yield of ^{210}At is 5–15%. This is due to the incomplete separation of astatine from bismuth in the gas phase at 600°C. At a higher temperature bismuth starts to distil.

It has been suggested[30] that the retention of astatine in the bismuth target is due to the formation of involatile compounds of it with bismuth inside the target irradiated with α-particles. This is confirmed by the fact that distillation at 700–800°C in air leads to the removal of up to 80% of the astatine from the bismuth target[30]. Evidently on heating in air the compound of bismuth with astatine decomposes with the formation of bismuth oxide and free astatine. From these results Appelman[45] developed the following scheme for the separation of astatine from the bismuth target.

The irradiated bismuth target is put in a stainless steel beaker and heated to 270°C to remove volatile impurities. The subsequent distillation of the astatine is carried out at 800°C. The distillate is collected on a water-cooled platinum plate suspended above the molten target. For the final purification of the astatine the platinum is put in a quartz tube and the impurities are removed at 130°C and a pressure of 10^{-4} mmHg, after which the astatine is redistilled at 500°C. The pure astatine is condensed in a

† When the astatine is produced by deep fission or irradiation of thorium by high-energy protons, such precautions are not needed since usually the intensity of the beam of protons is not so great as to cause strong overheating of the target. [It appears that the terms "deep fission" and "division" used in this review refer to *fission* and *spallation* respectively of Western literature (see especially Ref.50) (Ed. of Translation)].

U-tube cooled with dry ice. The astatine is washed from the walls of the tube with 0.5 ml dilute nitric acid. In this instance the yield reaches 30% and the concentration of astatine in the solution is $\sim 10^{-8}$ M.

The distillation method is also used for the separation of astatine from other targets, for example, gold[46]. Here the irradiated target is dissolved in molten lead or bismuth, after which the astatine is distilled off.

In addition to distillation, astatine is also separated from the target by the so-called "wet method". In this the irradiated bismuth or bismuth oxide can be dissolved in perchloric acid containing a little iodine as a carrier for the astatine, and the bulk of the target is thrown out of solution by precipitating bismuth phosphate. The astatine passes into the filtrate at AtI[47]. However, the preparation contains some polonium.

Neuman[48] made use of its extractibility by isopropyl ether for the separation of astatine from bismuth. The bismuth target is dissolved in nitric acid, the solution evaporated, but not to dryness, since a little nitric acid does not interfere with subsequent operations, and concentrated hydrochloric acid is added to bring the solution of 8 M in HCl. Then the solution is cooled and the astatine extracted with isopropyl ether, saturated with 8 M HCl. The organic phase is washed with 8 M HCl and then the astatine is back-extracted by NaOH solution containing a little iron(III). Iron hydroxide retains the remaining impurities completely and the loss of astatine here does not exceed 5%. The yield is $\sim$ 90%.

An interesting method of extraction separation of astatine from polonium and bismuth has been described[30]. The extractant used to separate astatine from concentrated hydrochloric acid solutions is di-isopropyl ether containing a little of a 20% solution of tributyl phosphate in isobutyl ether, and the extraction was effected in the presence of iron(II) as a reductant. Traces of polonium, bismuth, and lead are washed out of the organic phase by a mixture of 2 M nitric and 4 M hydrochloric acid. The back-extraction is carried out with alkali.

In the production of astatine by the deep fission of thorium the formation cross-section of the isotopes of astatine is two or three orders of magnitude less than the total formation cross section of the products of division and deep fission[49,50]. In the present instance to obtain radiochemically pure astatine effective purification from most of the elements of the Periodic System is necessary.

A method for separating astatine from lead, bismuth, and thorium irradiated with high-energy protons has been described[23]. According to this method, 1 g metallic thorium irradiated with protons of 660 MeV energy, is dissolved in 5 ml concentrated nitric acid by heating in a flask with a reflux condenser. 40 ml 8 M hydrochloric acid saturated with chlorine are added to the nitric acid solution. The extraction is performed with 60 ml di-isopropyl ether in an extractor with a mechanical stirrer. The organic layer is washed twice with 15 ml 8 M hydrochloric acid. The astatine is back-extracted from the ether with 40 ml 0.1 M solution of sodium stannite in 2 M NaOH. 10–15 mg sodium tellurite, 4–5 mg lanthanum chloride, and 1–2 mg sodium chloroaurate were added to the alkaline solution. The solution is separated from the residue by filtration through a glass filter. The precipitation of tellurium with sodium stannite is repeated twice. In this way polonium, gold, mercury, and several other metals which are co-precipitated with metallic tellurium from the alkaline solution in the presence of a reductant or of difficultly soluble hydroxides which are formed are separated from the solution. The alkaline filtrate is acidified with 20 ml concentrated hydrochloric acid containing $\sim$ 4 mg tellurium. The precipitation of tellurium, and astatine with it, from acid solution is carried out with vigorous mixing. After coagulation of the precipitate 5 mg tellurium are twice added to complete the precipitation of the astatine. The precipitate of tellurium containing the astatine is separated from the solution by centrifuging, washed with 6 M hydrochloric acid, and dissolved in a few drops of concentrated nitric acid. 20 ml 6 M hydrochloric acid is added to the solution obtained and the tellurium precipitated with tin(II) chloride. After coagulation of the precipitate the precipitation of tellurium (5 mg) is repeated once more. The precipitate is centrifuged off, washed with concentrated acid and dissolved in 5 ml 8 M HCl whilst passing gaseous chlorine. The astatine is separated from the tellurium by extraction into di-isopropyl ether. The ethereal layer (6 ml) is washed twice with 1.5–2 ml 8 M hydrochloric acid and the astatine is re-extracted with water (twice with 5 ml). After extraction a solution of radiochemically pure astatine is obtained $\sim$ 0.01 M in HCl and containing traces of solvent is obtained.

To separate astatine from tellurium and to obtain a concentrated preparation the chromatographic method can be used[51]. A solution of 8 M HCl saturated with chlorine which contains tellurium and astatine is passed through a layer of Dowex 50 × 8 cation-exchange resin. The tellurium is not retained on the resin; the astatine is adsorbed and is subsequently eluted with chlorine water. The yield of astatine in this method is 60 ± 10%, the degree of purity $\sim 10^{7}$.

Lefort and coworkers[22,52] give the following scheme for the separation of astatine which is formed as a result of the fission of ^{232}Th under the action of protons with energy 160 MeV. The thorium target is dissolved in concentrated hydrochloric acid with the addition of small amounts of hydrofluoric acid. The solution is diluted to 3 M HCl and the astatine coprecipitated by tin(II) chloride with elemental tellurium. To remove the polonium coprecipitated during this the tellurium is dissolved by heating in the minimal quantity of concentrated nitric acid and again precipitated with a milder reductant—sulphur dioxide from dilute hydrochloric acid solution. The precipitate, which contains the astatine, is dissolved in a little concentrated nitric acid, made alkaline until 2 M in NaOH; the astatine is separated from the tellurium and traces of polonium and other radioactive contaminants during their coprecipitation with elemental tellurium after addition of sodium stannite. The filtrate is acidified with nitric acid to 0.3–0.5 M. To prevent the capture of astatine by colloidal tin at the moment of change of the acidity of the medium, small portions of hydrofluoric acid are added. Astatine is isolated from the acid solution by spontaneous deposition on silver foil. This gives an α-radioactively pure preparation of astatine. To bring the astatine into solution, the silver foil is dissolved in concentrated nitric acid and the silver precipitated as chloride. To avoid retention of astatine by the silver chloride precipitate, the latter operation is done in a darkened place.

5. PHYSICAL PROPERTIES OF ASTATINE

Owing to its short half-life, astatine cannot be obtained in ponderable amounts; because of this the physical properties of this element and of its compounds have been incompletely studied. The information was mainly obtained by interpolation and extrapolation of data for its nearest analogues or on the basis of theoretical calculations.

The predicted melting and boiling points are 411° and 299°C respectively [53] [sic (Ed. of Translation)]. The radius of the At^{7+} ion calculated on the basis of theoretical data is 0.62 Å. [54] The crystalline ionic radius of At^- evaluated by several investigators [55-57], is close to 2.3 Å. The radius of At^- in gaseous molecules is calculated to be [57] 1.97 Å. Calculations of the ionisation potentials give the following values: first 9.6, [58-60], second 18.2, [58-59], third 30, fourth 41, fifth 51, sixth 78, and seventh 91 eV. [59]

The relative electronegativity of the astatine atom is estimated [61] to be 2,2 and the atomic refraction, calculated on the basis of this quantity, is 19.3 cm^3. [62]

Starting from the well-known data on the vibration frequencies of the diatomic molecules F_2, Cl_2, Br_2, and I_2, this quantity was also found by extrapolation for At_2 ($\omega_e \simeq 160\ cm^{-1}$). [60] The graphical dependence of ω_e plotted on the coordinates $\lg \omega_e$ against $\lg n^2 I$ (where n is the principal quantum number, and I the ionisation potential of a molecule of type XX) gives for At_2 a value $I(At_2) = 8.3$ eV. The dissociation energy of an astatine molecule $D(At_2)$, found by a similar method, is 1.2 eV. In the same study [60] the dissociation energy of an ionised astatine molecule $D(At_2^+)$ was found to be 2.4 eV by use of a thermodynamic cycle. By calculations, some thermodynamic characteristics were obtained for atomic astatine [57,63], for At_2 molecules [64], and for several compounds of astatine with alkali and alkaline earth elements [57-63].

It should be noted that although many chemical and thermodynamic parameters have been calculated for a diatomic astatine molecule, the At_2 molecule was not detected in extremely thorough experiments made by a mass spectrometric method [65].

The most modern equipment now allows several physical constants of astatine to be determined experimentally using indicator amounts of the element. For example, the absorption spectrum of astatine was investigated with the aid of a highly sensitive spectrograph with a capillary absorption cell and use of gaseous specimens of astatine weighing 0.2 mg. [66]

Two lines were observed with wavelengths 2244.01 and 2162.25 Å, and were assigned respectively to the transitions

$$6p^5\ ^2P^0_{3/2} - 6p^4\ 7s^4\ P_{5/2} \text{ and } 6p^5\ ^2P^0_{3/2} - 6p^4\ 7s^4 P_{3/2}. \qquad (E)$$

6. CHEMICAL PROPERTIES OF ASTATINE

As noted above, astatine does not have long-lived isotopes, in consequence of which only ultra-small amounts of the element are available for studying its properties. The investigation was mainly carried out with concentrations of 10^{-11}–10^{-15} M. The most concentrated solution of astatine (10^{-8} M) was obtained by Appelman [45]. It is known that 650 atoms of astatine lead to one α-decay per minute. For this reason a 1 M solution would exhibit an activity of 1.54×10^{16} α-particles min^{-1} cm^{-3}. At such a high specific activity an effervescence of the solutions being tested would be unavoidable and there would be intensive radiolysis of the water with the formation of considerable quantities of hydrogen peroxide. Under these conditions it would be impossible to stabilise the astatine in a desired oxidation state. Astatine, like any other element, present in ultra-small concentrations, must react with traces of impurities in the solutions, be sorbed on dust particles to form radio-colloids, etc.

Usually in studying the behaviour of an element present in indicator amounts the carrier method is used. But astatine does not have either stable isotopic carriers or a sufficiently satisfactory non-isotopic carrier. Being the heaviest element of the halogen subgroup it should exhibit the properties of the latter. However, astatine shows electronegative properties more rarely than iodine, and in some instances it is reminiscent of a metal. The position is greatly complicated by the fact that the chemistry of trace amounts of iodine differs greatly from the chemistry of its macro-quantities [67-69]. At low concentrations iodine not only forms new species (for example, in the oxidation of iodide by Cr^{VI} or Ce^{IV} at iodide concentrations of $\sim 10^{-7}$ M in 1 M sulphuric acid three unidentified iodine species unknown in the macrochemistry of iodine were found), but its interaction with traces of dust and micro-impurities was noted [70].

Four states of oxidation of astatine are now known: At^- the astatide ion, At^0 the zero state, At^X some unidentified valence state, and At^{5+} in the form AtO_3^-. Appelman [71] gives the following scheme for the redox potentials of astatine at pH = 1:

$$At^- \xrightarrow{-0.3\,V} At^0 \xrightarrow{-1.0\,V} At^X \xrightarrow{-1.5\,V} AtO_3^- \xrightarrow{-1.6\,V} H_5AtO_6\ (?)$$

1. Astatine in the Zerovalent State, At^0

Like elemental iodine, astatine in the zerovalent state of oxidation exhibits very high volatility. On this property, in particular, is based the method of isolating astatine from a fused bismuth target.

In the gaseous state astatine is readily sorbed by surfaces of various materials. Table 2 shows data on the simultaneous adsorption of astatine on the surfaces of various metals in a high vacuum [44]. In each instance the surface of the metals was previously purified by heating at ~ 400°C in an atmosphere of hydrogen.

Table 2.

Metal	Quantity of adsorbed astatine, relative %		
	20°	325°	
		expt. 1	expt. 2
Aluminium	0.3	0.2	0.3
Nickel	0.2	0.6	0.7
Copper	0.5	0.6	4.3
Platinum	36.3	33.5	6.5
Gold	38.4	0.1	0.7
Silver	24.3	65.0	87.5
	100.0%	100.0%	100.0%

The vaporisation and adsorption of astatine depends on the nature of the substrate. The low volatility from the surface of gold and platinum is evidently explained by the formation of a new valence form of astatine or its reaction with the material of the substrate [44].

Astatine in the zerovalent state in solutions cannot be identified with any definite chemical species. This can be the products of the reaction of astatine with traces of organic impurities, interhalogen compounds of astatine, and elemental astatine [45]. The latter is undoubtedly present in dilute nitric acid solutions. This happens although

a considerable amount of astatine is lost during the evaporation of the solution. In the drying of a nitric acid solution on platinum substrates ~26% of the astatine volatilises[44]. However, the loss of astatine due to its volatility is not so great as the loss of iodine during the evaporation of the solutions which contain micro-amounts of elemental iodine. The retention of astatine on various surfaces during the evaporation of aqueous solutions varies with the nature of the surface, the composition of the solution, and the conditions of evaporation[15].

Sorption on glass from dilute nitric acid solutions is inherent to astatine in the zerovalent state[45]. An increase in the nitric acid concentration leads to a decrease in sorption, probably as a result of a change in the valence state of the astatine[45].

At^0, like elemental iodine, is extracted very well from nitric acid solutions by almost all organic solvents. This property of astatine is widely used in studying its chemistry. Observation of the change in extraction coefficients of astatine from HNO_3 solutions with change in the concentration of the latter on adding other acids, complex-formers, or various oxidants and reductants makes it possible to find the form of the compound extracted, the degree of complex formation, and the oxidation potential.

At^0 is completely extracted from the organic phase on shaking with 0.1 M NaOH. Probably in this instance the At^0 disproportionates to astatide and a higher oxidation state[44]. Acidification of the solution converts astatine into its initial state and it is again extracted by organic solvents with the initial partition coefficient.

At^0 is partly coprecipitated from aqueous solutions with some hydroxides and also with AgI and TlI, probably as a result of its sorption by the developed surface of these precipitates. Increasing the acidity of the solution completely suppresses the adsorption. Washing the AgI and TlI precipitates with acetone completely removes the astatine from their surface.

Astatine(0) can be isolated from solution by precipitation with elemental tellurium, metallic silver, and on various heavy metal sulphides[18,72]. It is also coprecipitated with PdI_2.[47]

Study of the electrochemical behaviour of astatine showed that the critical potential for the deposition of At^0 from nitric acid solutions on a cathode is −1.22 V and at the anode −1.45 V[44] [Both potentials referred to a normal hydrogen electrode (Ed. of Translation)]. Thin gold foils were used as electrodes in these experiments.

The nature of the astatine compounds liberated in electrolysis is unknown.

The extraction of astatine by polar solvents from solutions of mineral acids in the presence of oxidants or reductants is widely employed in studying the chemistry of astatine[44,45,48,73] but the distribution coefficients for At^0 between aqueous and organic phases depend quite strongly on the purity of the reagents used. Impurities, even those found in micro-concentrations, can bring a considerable part of the astatine into a form with another distribution coefficient. Thus, the repeated extraction of astatine from the same solution with an organic solvent leads to a fall in the partition coefficient with each extraction and finally the astatine stops being extracted. Similarly for repeated re-extraction from an organic phase by an aqueous solution the amount of astatine re-extracted falls[44,45]. Consequently in using extraction as a method of studying the chemistry of astatine, conclusions can be drawn about the change in the state of the latter only when there are very large differences in the partition coefficients of the astatine forms being studied[15].

An important contribution to the study of the chemistry of astatine by the extraction method was made by Johnson and coworkers[44], Neumann[48], and Appelman[45,73]. During the action of reductants of the type of SO_2, H_3AsO_3, or metallic zinc on acid solutions which contain At^0 a sharp decrease in the partition coefficients was observed, evidently the astatine(0) is reduced to At^-, which is confirmed by its coprecipitation with silver or thallium iodides. With Br_2 astatine is oxidised to an unidentified valence state[45].

The addition of strong oxidants of the $S_2O_8^{2-}$ type converts astatine into AtO_3^-, which is coprecipitated with $AgIO_3$.[44]

2. Astatide Ion

The astatide ion is the most studied state of astatine because this form is the most similar in properties to the iodide ion. At^- is formed in solutions which contain astatine(0) in the presence of strong reductants such as SO_2, H_3AsO_3, hydrogen at the moment of liberation in acid solution, or Na_2SO_3 in alkali. This is shown by the results of experiments on electromigration and on coprecipitation with iodides at any acidities and in the presence of various anions[18,44]. At^- is not removed from precipitates of insoluble iodides on washing them with acetone (as happened in the coprecipitation of At^0). These results show that At^- is isomorphously coprecipitated with iodides.

The ratio of the diffusion coefficients of I^- and At^- in 1% NaCl solution which contains 1.2×10^{-3} M KI and 4×10^{-3} M Na_2SO_3 is $D_{I^-}/D_{At^-} = 1.41 \pm 0.02$.[74]

It is thought that the astatide ion absorbs ultraviolet radiation of wavelength ~3000 Å.[75]

The work with At^- in acid solution must be carried out with great precaution since there are indications of the formation of volatile astatides[18,44].

3. The Unidentified Valence State At^X

Oxidants such as the vanadate ion, bromine, chlorine, dichromate, concentrated nitric acid, and Fe^{3+} ions oxidise At^0 to some valence form the state of oxidation of which lies between At^0 and AtO_3^-.[15,44,45] This form is not extracted by carbon tetrachloride and is not coprecipitated with iodides.

Some investigators ascribe to this state of astatine the charge 3+,[76] others the form AtO^- [77,78] (by analogy with iodine) or AtO_2^-.[78] Although the existence of the latter for iodine is also not established, this form could be more stable for astatine[76].

The main regularities in the change in the properties of the elements in the Periodic System show that astatine ought to be more "metallic" than the other halogens. This signifies, in particular that astatine should acquire a positive charge more readily than iodine. In several studies it was found that in its properties astatine shows more resemblances to polonium and bismuth—its nearest neighbours in the Table—than to iodine[18,79].

Experimental results have been obtained[44] which show the reversibility of the electrochemical deposition of astatine on a gold cathode from sulphate solutions oxidised with dichromate, which can be held as proof of the existence of astatine in the form of a cation.

The investigation of the behaviour of astatine oxidised by dichromate in solutions of nitric acid showed that it is present as a singly-charged cation[80]. This was shown by experiments on migration, from the results of which it is clear that the astatine ion in this medium moves predominantly towards the cathode[80]. It appeared that astatine in

this form is sorbed on monofunctional sulphonic-cation-exchange resins. This allowed the charge on the ion of astatine oxidised by dichromate in nitric acid solutions to be determined, and it was found to be unity[80].

In a series of chemical properties the astatine cation is similar to the heavy singly-charged cations, for example, thallium and caesium, and is absorbed well by precipitates of caesium tungstophosphate, thallium dichromate, and silver iodate (Table 3)[81,82].

The astatine cation is spontaneously deposited on metallic platinum coated with an oxide film (Fig. 2).[83] The rate of deposition (at a time of deposition $\tau \leqslant 40$ min) is satisfactorily described by the equation for a first-order reaction:

$$\frac{dx}{d\tau} = K(a - x)\frac{S}{V}$$

where a is the initial amount of the element in the solution, S the surface of the platinum, V the volume of solution, and K a constant.

Table 3. Retention of the singly charged astatine cation by various precipitates from nitric acid solutions containing the dichromate ion. (0.005 M $H_2Cr_2O_7$) (solution volume 5 ml).

Precipitate and its weight	Process of retention of astatine	Composition of solution over precipitate (other than dichromate ion)	Astatine in ppt., %
$Tl_2Cr_2O_7$ 20 mg	retention at moment of formation of ppt	2 M HNO_3	94 ± 5
ditto	ditto	2 M HNO_3 + 10 mg/ml La^{3+}	94
»	sorption on existing ppt	2 M HNO_3	84 ± 1
»	ditto	2 M HNO_3 + 10 mg/ml La^{3+}	80 ± 5
$Ag_2Cr_2O_7$ 40 mg	retention at moment of formation of ppt	2 M HNO_3	74 ± 6
ditto	sorption on existing ppt	ditto	4.5 ± 1.5
$AgIO_3$ 15 mg	retention at moment of sorption formation of ppt	0.5 M HNO_3 + 0.01 M KIO_3	96 ± 1
ditto	ditto	0.5 M HNO_3 + 0.01 M $AgNO_3$	91 ± 2
$Ba(IO_3)_2$ 40 mg	»	0.5 M HNO_3 + 0.02 M KIO_3	95
ditto	»	0.5 M HNO_3 + 0.02 M $Ba(NO_3)_2$	59 ± 4
$Th(IO_3)_4$ 40 mg	»	0.5 M HNO_3 + 0.01 M KIO_3	47 ± 5
ditto	»	0.5 M HNO_3 + 0.01 M $Th(NO_3)_4$	9.5 ± 1.5
Cs_2HPW^* 100 mg	sorption on existing ppt	3 M HNO_3	6 ± 0.5
Cs_3PW^* 100 mg	ditto	3 M HNO_3	78 ± 4
ditto	»	3 M HNO_3 + 0.3 M $CsNO_3$	87 ± 0.2
Rb_3PW^* 100 mg	»	3 M HNO_3 + 0.3 M $RbNO_3$	74 ± 1
$(NH_4)_3PW^*$ 100 mg	»	3 M HNO_3 + 0.3 M NH_4NO_3	24 ± 4

* $(PW)^{3-} = [P(W_{12}O_{40})]^{3-}$.

The adsorption is affected positively by raising the temperature and negatively by increasing the acidity. The astatine deposited on the platinum is held strongly on the metal surface. However, it can be easily desorbed by anodic polarisation of the platinum.

The spontaneous liberation of astatine at platinum covered with an oxide film with subsequent anodic dissolution allows solutions of astatine to be obtained in almost all strong acids, and, moreover, opens the possibility of using this phenomenon in the production of radiochemically pure astatine[83].

4. States 5+ and 7+

The existence of an astatate ion (AtO_3^-) was inferred on the basis of the results of experiments on the coprecipitation of astatine with silver, lead, and barium iodates from nitric and hydrochloric acid solutions containing strong oxidants: $S_2O_8^{2-}$, Ce^{IV}, IO_4^-, $NaBiO_3$.[44,73] The astatate ion is not extracted by carbon tetrachloride or benzene. The negative charge of this form of astatine produced in oxidation by $Na_2S_2O_8$ in nitric acid was shown by electromigration experiments[44]. It was found[44] that astatine oxidised by a hot $Na_2S_2O_8$ solution is coprecipitated very well with

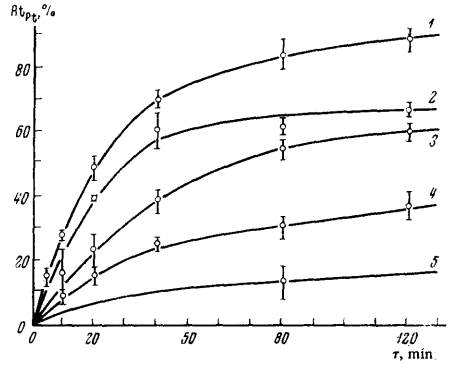


Figure 2. Liberation of astatine at platinum from nitric acid solutions as a function of time. Temperature 23°C; $[H_2Cr_2O_7] = 5 \times 10^{-3}$ M; $S_{Pt} = 4$ cm^2; $V_{soln} = 10$ ml; HNO_3 concentration, M: *1*) 1; *2*) 3; *3*) 5; *4*) 7; *5*) 10.

lanthanum hydroxide. It is assumed that in this instance a compound of the type $La(AtO_3)_3$ insoluble in alkaline medium, is formed.

However, Appelman[72] did not observe the coprecipitation of astatine oxidised by Ce^{IV} in 6 M $HClO_4$ with cerium(IV) hydroxide. It is reported[84] that astatine oxidised by Ce^{IV} is readily extracted by di-isopropyl ether from 4–5 M solutions of nitric, sulphuric, and perchloric acids. Under these conditions micro-amounts of iodine are not extracted. It is known that Ce^{IV} in solutions of strong mineral acids oxidises iodine in indicator amounts to IO_3^-.[67]

Experimental results proving the existence of At^{7+} as perastatate do not exist at present.

Thus Appelman[71], using vigorous oxidants such as H_5IO_6 or Ce^{IV} in 6 M $HClO_4$ did not obtain astatine in a form coprecipitable with potassium periodate. And under these conditions astatine is retained solely by iodates. However, bearing in mind the various forms of periodates[85], a definite conclusion about the absence of a 7+ state cannot be drawn without further studies.

All the above valence states of astatine are formed, as already noted above, at such low concentrations that to stabilise these forms it is necessary to hold the oxidation potential of the solution within strictly defined limits. Therefore to study the chemical properties of any state of astatine the solution must contain an oxidant (a reductant, for the astatide ion), not only for converting the astatine into the required form but also for protecting this form at the time of the experiment from micro-impurities which are unavoidably present in the reagents used.

5. Interhalogen Compounds of Astatine

In studying the chemistry of astatine in solutions which do not contain stabilising agents irreproducible results are

usually obtained. When the stabilising buffer is the halogen pair I^-/I_2, the predominant state will be interhalogen compounds of the types AtI and AtI_2^-. In the presence of elemental iodine the zero valency of the element is represented exclusively by AtI molecules. For the last instance Appelman[73] determined with great accuracy the value of the partition coefficient between carbon tetrachloride and water, 5.5 (Table 5).

Detailed studies have been made[23,48] of the extraction of astatine by di-isopropyl ether from chlorine-treated hydrochloric acid solutions of various concentrations (Fig. 3). On the basis of the results of extraction experiments Neumann[48] drew conclusions about the existence of chloroastatates of composition $AtCl_2^-$ or $AtCl_4^-$. In his review[77], Bagnall states that the composition of the complex probably corresponds to the formula $AtCl_2^-$, that is, the astatine is in oxidation state +1.

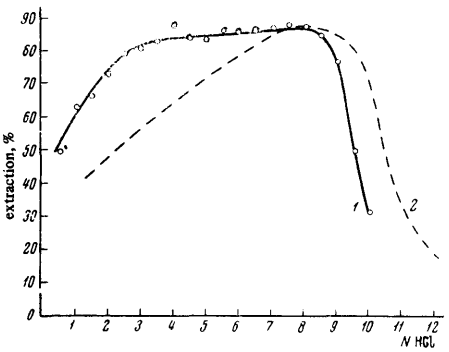


Figure 3. Extraction of astatine from hydrochloric acid solutions by di-isopropyl ether:
1) after the results of Belyaev and coworkers[23]; *2*) after the results of Vinogradov and coworkers[48].

This assumption found confirmation in a study of the adsorption of the astatine cation on platinum covered with an oxide film[83] from nitric acid solutions as a function of the chloride ion concentration. It was found that chloride ion has a negative effect on the adsorption of astatine on platinum (Table 4).

The distribution of astatine between the solution and the platinum depends on the chloride ion concentration:

$$(K_d D - 1) = \frac{1}{K_n}[Cl^-]^n$$

where $K_d = At_{Pt}/At_{soln}$ is the ratio of the amount of astatine on platinum (At_{Pt}) to the amount of (At_{soln}) in solutions which do not contain chloride ion, $D = At_{soln}/At_{Pt}$ the ratio of the amount of astatine in the solution to the amount of it on the platinum in the presence of chloride ion, and K_n the instability constant of the most stable chloro-complex of astatine with n ligands.

In the graph of $\lg(K_d D - 1)$ against $\lg[Cl^-]$ the points calculated from the results in Table 4 lie along a straight line with a slope of 2. Paper electromigration shows that under these conditions astatine is present in an anionic form[81,83]. These results suggest the singly-charged astatine cation adds two Cl^- ions to form an anionic complex of type $[(AtX)Cl_2]^-$. The stability constant of this complex is $(7.4 \pm 0.8) \times 10^5$ M^{-2}‡.

The anionic chloro-complex exhibits one property which is very interesting from the preparative point of view: it is adsorbed on sulphonic cation-exchange resins of the type of KU-2§ and Dowex 50 from solutions of hydrochloric acid and alkali metal chlorides first saturated with chlorine (Fig. 4).[51]

The interhalogen compounds of astatine in various systems in the presence of iodine with the use of liquid extraction by carbon tetrachloride was studied in detail by Appelman[45,73]. Table 5 gives the partition coefficients of the halogens and interhalogen compounds between carbon tetrachloride and the aqueous phase.

On the basis of the distribution results Appelman[45] calculated the formation constants of various astatine complexes (Table 6).

Table 4. Deposition of astatine on platinum in the presence of hydrochloric acid from 1 M HNO_3–5 x 10^{-3} M H_2CrO_4. $S_{Pt} = 4$ cm^2; $V = 10$ ml; $\tau = 40$ min.

[HCl], M	%At on Pt	[HCl], M	%At on Pt
0	53.7±31	$8 \cdot 10^{-3}$	2.1±0.12
$2 \cdot 10^{-3}$	23.5±2.8	$1.3 \cdot 10^{-2}$	0.91±0.13
$3 \cdot 10^{-3}$	12.5±2	$2 \cdot 10^{-2}$	0.52±0.2
$5 \cdot 10^{-3}$	4.9±0.3		

It is interesting to note that astatine always forms a more stable complex than iodine under analogous conditions. The formation constants of identical interhalogen complexes of astatine and iodine differ by a factor of 5–8.[45]

It is well known that molecules which consist of two identical halogen atoms are extracted by carbon tetrachloride considerably better ($D_{I_2} = 86$) than molecules which contain two different atoms ($D_{AtI} = 5.5$, $D_{IBr} = 4.3$, $D_{ICl} = 0.34$). This is because the molecules of the first type are completely non-polar, whereas the interhalogen compounds are dipoles.

The coprecipitation of AtI with elemental iodine in chloroform solutions has been studied[86]. It was shown that the introduction of AtI into iodine crystals obeys Dorner and Hoskins' logarithmic law of distribution. The partition coefficient is

$$\lambda = \frac{\lg(AtI_{soln})/(AtI_{soln} + AtI_{solid})}{\lg(I_{2soln})/(I_{2soln} + I_{2solid})} = 4.$$

Interhalogen compounds are formed in the solid state[87]. Thus CsI_3 which contains $CsAtI_2$ is easily obtained on adding an excess of solid iodine to an aqueous solution of CsI(At). When the system is heated and then cooled, CsI_3 containing astatine is obtained.

‡ When this article was being prepared for press the stability constants of this complex were checked and defined more accurately by the cation-exchange method and β_2 was found to be 2.5×10^5 M^{-2}; moreover, the same method was used to determine the stability constant of a chloro-complex with one ligand, $\beta_1 = 7 \times 10^2$ M^{-1}.[33a]

§ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

The thermal decomposition of $CsAtI_2$ obeys the general rule for the decomposition of polyhalogen compounds (in such instances an involatile monohalide is formed—the lighter halogen with the metal), that is, involatile CsI is formed and the astatine is volatilised in the form AtI.[88]

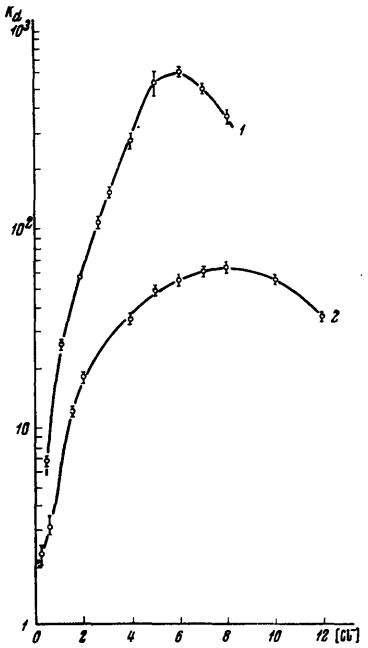


Figure 4. Distribution of astatine, oxidised by chlorine, between the sulphonic cation-exchange resin Dowex 50 x 8 and a solution, as a function of the concentration: *1*) LiCl; *2*) HCl.

Table 5.[73] Partition coefficients of the halogens and interhalogen compounds (21°C), $D = (XY)_{CCl_4}/(XY)_{aq}$.

XY	D	XY	D
AtBr	0.040	AtI	5.5
ICl	0.34 (25°)	Br_2	27
IBr	4.3	I_2	86

Table 6.[45] Formation constants of the various interhalogen complexes of astatine.

Reaction	K_{form} ± 10% (21°)
$At I_{aq} + I^- = AtI_2^-$	2000
$At I_{aq} + Br^- = AtIBr^-$	120
$At I_{aq} + Cl^- = AtICl^-$	9
$AtBr_{aq} + Br^- = AtBr_2^-$	320
$At I_{aq} + IBr_{CCl_4} = AtBr_{aq} + I_{2CCl_4}$	3800
$At I_{aq} + \frac{1}{2}Br_{aq} = AtBr_{aq} + \frac{1}{2}I_{2aq}$	4.2×10^4
$AtICl^- + Cl^- = AtCl_2^- + I^-$	2×10^{-4}

7. ASTATINE IN ORGANIC COMPOUNDS

A rather large number of organoelemental compounds of iodine have now been obtained and their properties studied in more or less detail. This cannot be said about astatine although the existence of stable alkyl and aryl derivatives of this element follows from its position in the Periodic System (the stability of organic derivatives in Periodic Group VII corresponding to valencies of +3 and over increases from chlorine to iodine).

The difficulty encountered in working with the inorganic forms of astatine is greatly increased in studying the organic derivatives of this element.

One of the features of the preparation of organoelemental compounds of radioactive elements is that they can be produced only with vanishingly small amounts of materials. This is due on the one hand to the impossibility of obtaining ponderable amounts of individual radioactive elements (francium, astatine, radon) even with the aid of modern equipment, and of the necessity of using special, quite complicated techniques of investigation. On the other hand, and this is most important, the undertaking of investigations with considerable amounts of certain radioactive substances is accompanied by such radio-chemical changes (both in the substances studied and in the surrounding medium), which rules out the possibility of obtaining correct information about the properties and state of the substances being studied.

One of the important consequences of the fact that in the preparation of organoelemental compounds of the radioactive elements one is dealing with submicro-amounts of substance is the impossibility of finding the qualitative and quantitative composition of the compounds being studied by direct methods of analysis. For this reason indirect methods based on a comparison of the behaviour of the substance being studied with that of known compounds of analogous elements play the determining role in such investigations. Here the most convenient method is observation of the chromatographic behaviour of the elements and their compounds.

Since astatine does not have long-lived isotopes, almost the only method of making its organic derivatives is preparation with a non-isotopic carrier—iodine.

Until recently only a few papers[48,78,89-91] had been published on the preparation of organoastatine compounds.

From data on the extraction of astatine in an intermediate state of oxidation from 0.5 M sulphuric acid with benzene and a 10^{-3} M solution of phenol in carbon tetrachloride and the back-extraction of astatine from these solvents with 0.5 M NaOH, Neumann draws conclusions about the existence of astatobenzene and astatophenol[48]. However, these compounds were not isolated and identified.

Contradictory results were obtained in an attempt to make iodo(astato)form and *p*-iodo(astato)aniline[78].

Aten's statement (based on the known chemical properties of astatine) that astatine is probably most readily introduced into an organic molecule when it is found in a positively charged state in some intermediate product obtained at the time of reaction merits attention[78].

A large number of organic compounds of astatine also of interest for biological investigations has been obtained[89-91]. Astatobenzene, astatinated serin albumen, and *p*-astatobenzoic acid were obtained through diazo-compounds. *p*-Astatobenzoic acid offers the possibility of introducing astatine into various proteins. Direct astatination in the presence of KI_3 gave astatinated egg albumin and γ-globulin and the reaction of astatine with *N*-iodosuccinimide gave astatinated tyrosine.

Methods of making astatinated compounds of the types RAt, $RAtCl_2$, R_2AtCl, and $RAtO_2$ (where R is phenyl or *p*-tolyl radical) have been described[92,93].

Both phenyl and *p*-tolyl derivatives of astatine were obtained by the same scheme:

$$R_2ICl + KI(At) \rightarrow R_2I \cdot I(At) \xrightarrow{170-180^\circ} RI(At) \xrightarrow{Cl_2} RI(At)Cl_2 \begin{cases} \xrightarrow{R_2Hg} R_2I(At)Cl \\ \xrightarrow[NaOCl]{} RI(At)O_2 \end{cases}$$

To prepare $RAtCl_2$, KI(At) solution was added to aqueous R_2ICl solution, to give a crystalline precipitate which was subjected to thermal decomposition at 170–190°C:

$$R_2I.I(At) \rightarrow 2RI(At).$$

A little chloroform was added to the reaction product and after cooling to 0°C the RI(At) was chlorinated until a yellow crystalline precipitate of $RI(At)Cl_2$ no longer separated.

$RI(At)Cl_2$ was used to make R_2AtCl. The crystals were dissolved in chloroform, the solution was heated to boiling and a hot chloroform solution of R_2Hg was slowly added to it. The mixture was heated for several minutes on the water-bath and then cooled. The precipitate was centrifuged off and R_2AtCl was extracted with water from the mixture of products remaining in the solution.

Table 7. Value of R_f for the tolyl derivatives of astatine and iodine in the chromatographic of various solvents on mixtures of silica gel KSM No.5 and gypsum. Fixed layer.

Substance	R_f				
	methanol	water-25% methanol	water-25% ethanol	butanol	acetone
p-$CH_3C_6H_4ICl_2$	0.33±0.02	0.1±0.01	0.68±0.02	0.6±0.02	0
p-$CH_3C_6H_4AtCl_2$	0.32±0.03	0.11±0.02	0.68±0.04	0.61±0.03	0
$(p$-$CH_3C_6H_4)_2ICl$	0.1±0.02	0.23±0.02	0.1±0.03	0.67±0.02	0.55±0.02
$(p$-$CH_3C_6H_4)_2AtCl$	0.1±0.05	0.25±0.03	0.1±0.04	0.68±0.03	0.54±0.03
p-$CH_3C_6H_4IO_2$	0.65±0.05	0	0.75±0.04	0	0
p-$CH_3C_6H_4AtO_2$	0.65±0.05	0	0.72±0.05	0	0

To prepare $RAtO_2$, crystals of $RI(At)Cl_2$ were put in a centrifuge tube, to which were added 2 ml 50% NaOH solution and 0.5 ml acetic acid. The mixture was heated to 70°C and chlorinated to complete conversion of the yellow crystalline precipitate of $RI(At)Cl_2$ into a white amorphous precipitate of $RI(At)O_2$. Then the temperature was raised to 100°C, the precipitate rapidly centrifuged off, and on cooling the solution to 0°C $RI(At)O_2$ crystallised out.

The compounds obtained were identified by thin layer and paper chromatography.

The results of the analysis of the organoastatine compounds agree well, within the limits of error of the experiment, with the results obtained in the analysis of analogous iodine compounds (Table 7).

In a study of the properties of astatinated derivatives a large part has undoubtedly been played by their preparation using a method based on the change of chemical state of the atoms during nuclear transformations. In this instance it is possible to obtain organic compounds of astatine without a carrier. This method, which has played a large part in studying the chemistry of organopolonium compounds[94,95], has not yet been extensively employed for astatine. Apparently this is connected with the difficulty of obtaining a corresponding organic medium containing radon—the initial substance from which "hot" atoms of astatine are formed as the result of *K*-electron capture.

8. BIOLOGICAL BEHAVIOUR OF ASTATINE

It has been found that astatine, like iodine, is selectively concentrated in the thyroid gland[96]. In this connection the study of the biological properties of astatine started immediately after its discovery[96]. For this purpose At^{211} is usually employed, for which, as noted above, any act of disintegration leads to the expulsion of an α-particle, and the daughter ^{207}Bi exhibits so great a half-life that it does not affect the results of the investigation. Preparations of astatine for biological purposes are obtained by a standard method: distillation in a vacuum from a bismuth target and condensation in a trap on a thin ice surface. After melting the ice, an aqueous solution of astatine in minimal volume is obtained. The physiological solution used in injections is prepared by the addition of the appropriate amount of sodium chloride to the aqueous solution of astatine.

In studying the biological properties of astatine very small quantities of it are usually employed ($< 10\ \mu C$). To obtain sufficiently precise information about the distribution of astatine in organisms a very precise analytical method of separating it from biological specimens is needed. This requirement is satisfied by the method of radiochemical determination in biological materials developed by Hamilton and coworkers[72]: the organic substance is destroyed by wet combustion with a mixture of perchloric and nitric acids (9 M $HClO_4$ containing 30 vol.% 16 M HNO_3). Subsequently the solution is evaporated until perchloric acid fumes appear (during which the nitric acid distils off completely), diluted with distilled water to 3 M in perchloric acid, and the astatine separated from this solution for recording by coprecipitation with metallic thallium or by sorption on a silver disk. The separation on silver requires less time (73.5% is sorbed in the first 10 min and 100% after the next 20 min) and this method is more suitable for the serial analysis of biological materials.

Investigation of the radiobiological properties of ^{211}At showed that the α-particles emitted in the disintegration of this isotope produce some decay in the tissues of the thyroid and, unlike iodine, do not harm the neighbouring parathyroid gland[97]. This shows that astatine is perhaps the only means of therapeutic treatment for enlarged thyroid gland.

The radiobiological action of α-particles of astatine on the thyroid gland is 2.8 times greater[98] than deeply penetrating β-particles of ^{131}I.

It has been found that propylthiouracil suppresses the concentration of iodine in the thyroid gland but with astatine the effect is the reverse—its concentration is observed when this preparation is introduced into rats[99].

It is interesting to note that when astatine is introduced in the form of a radiocolloid it is deposited mainly in the

liver[100]. This reflects the general tendency for most elements which are capable of forming colloidal solutions.

In comparing the metabolism of astatine and radioiodine it was found that their excretion by the stomach and kidney is almost the same. In other instances with the exception of the thyroid the metabolism of astatine is completely different from that of iodine. Even on the introduction of a lethal dose of astatine in the form of true solutions into rats and apes, morphological changes in organs and tissues other than the thyroid were not noted[101]. The observation of the accumulation of ^{211}At in the human thyroid in the breakdown of some of the functions of this organ also showed the absence of concentration of astatine in other organs[102].

On the repeated introduction of large doses of astatine into rats and apes their growth is stopped, probably as a result of a change in the functions of the thyroid secretions due to deficiencies of the thyroid hormones[103]. This could also explain the complete destruction of tumours of the mammary gland in rats on the repeated introduction of small doses of astatine[103]. In some studies it is stated that astatine is partly concentrated in the mammary gland[104].

When very large doses of astatine were introduced into rats over 26 months almost complete destruction of the thyroid gland and highly developed tumours of the mucous and mammary glands were observed[105].

The accumulation of astatine by the thyroid gland is under the control of the pituitary body, and leads to the suppression of the concentration of astatine in the thyroid[106]. It was also shown that the thiocyanate ion blocks the accumulation of astatine in the thyroid, probably by forming a sufficiently stable complex. Consequently the thiocyanate ion can be used to remove astatine from this organ[106].

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In conclusion it must be noted that the experimental difficulties associated with the study of the chemistry of astatine were evidently due to factors that are now understood: it does not have long-lived isotopes and consequently is found in amounts commensurate with accidental contamination. Reviews on the chemistry of astatine[15,76-79,107-113] appear more frequently than original studies. A recently published paper[114] gives information about the [half-life] periods and α-particle energies of the lightest isotopes of astatine.

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Physicochemical Properties and Structure of Complex Compounds of Aluminium Hydride

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CONTENTS

I. Introduction	99
II. Complexes of aluminium hydride $AlH_3.nL$†	99
III. Alkali metal tetrahydroaluminates $MAlH_4$ and their complexes $MAlH_4.nL$	101
1. Methods of preparation of $MAlH_4$	101
2. Solubility and complex formation	102
3. Some reactions of tetrahydroaluminates	104
IV. Structure of the complexes $AlH_3.nL$ and $MAlH_4.nL$	104
V. Electrochemistry of systems containing aluminium hydride	109
1. Electrical conductivity of solutions of $MAlH_4$	109
2. Electrode processes	111

I. INTRODUCTION

Thanks to the diverse properties of solvents the electrochemistry of non-aqueous solutions allows processes which are inaccessible for study in aqueous solutions to be brought about and investigated. In particular, there is considerable interest in the experimental investigation of the anodic discharge of hydride hydrogen. The corresponding cathodic process in aqueous solutions—the discharge of H^+—has been studied rather fully. In the investigation of an anodic process it is sufficient to operate with discharge of anions of the type $(M^{+m}H_n)^{-n+m}$, which are precisely what exist in non-aqueous solutions. Since the binding energy of H^- in an anionic complex can depend significantly on the medium, it follows that there are at least indications about the nature of the bonding of this anion with the solvent. The behaviour of the anode during polarisation is also essential —its solubility, the nature and properties of the soluble products which are formed, and in the absence of solubility the order of the strength of the bonding of atomic or molecular hydrogen at its surface. Interest in the process of the discharge of hydride hydrogen, which was first observed by Bardwell[1] for a melt of CaH_2 in KCl–LiCl eutectic and by Ziegler and coworkers[2] for non-aqueous solutions, stimulated us to differentiate AlH_3 and its complexes of the $MAlH_4$ type from the class of compounds $MAlR'_nR''_{4-n}$, the electrochemical properties of which were considered earlier[3]. It was interesting to review the properties, a knowledge of which is needed in investigating the discharge of hydride ions. From the practical viewpoint the solutions of such substances can be used both for the electrodeposition of aluminium‡, and also for obtaining solutions of aluminium hydride[6], the chemical preparation of which is rather complicated.

In the anodic discharge of the AlH_4^- ion, AlH_3 and H_2 should be formed. The subsequent behaviour of AlH_3 and its influence on the kinetics of the anode process depends on the interaction of AlH_3 with the components of the solution, that is, on the nature of the complex formation. We will therefore begin with consideration of the properties of the complexes of AlH_3. Hydroaluminates§ must formally be considered as complexes $AlH_3.MH$. However, they exhibit a series of characteristic differences from the complexes of AlH_3 with organic ligands and are of special interest for electrochemistry. Therefore an examination of several of their properties and methods of preparation is treated under a separate heading. A separate chapter is devoted to the important problem of the structure of the complexes of AlH_3, in which those of the type $AlH_3.MH$ are considered as a special case of the complexes $AlH_3.L$. Finally, the last chapter is devoted to the natural electrochemical properties of the aluminium hydrides.

II. COMPLEXES OF ALUMINIUM HYDRIDE $AlH_3.nL$

In the pure solid state AlH_3¶ is known only as a polymer. $(AlH_3)_x$ is a white involatile substance, usually not free from diethyl ether. Aluminium hydride is insoluble in inert solvents, but soluble with the formation of complexes and depolymerisation in tetrahydrofuran, dioxan, triethylamine[9], diamines[10], and methylcellosolve[11]. The ethereal solution of AlH_3 obtained from $LiAlH_4$ and $AlCl_3$ by the method of Finholt and coworkers[12], is unstable† and on standing it deposits an ether-containing polymer $(AlH_3)_x$[9,14–16], the composition of which depends on the conditions of isolation[9,12,15,17].

† Symbols used in the text: L ligand; M metal; R alkyl, halogen, or hydrogen; NR_3 tertiary amine; Hal halogen; μ dipole moment of the molecule in Debye units; t_b boiling point; t_f melting point; C.N. coordination number; κ electrical conductivity, $\Omega^{-1}\,cm^{-1}$. The thermochemical sign convention is used for denoting the thermal effects.

‡ Kessler and coworkers have reviewed the work of Brenner and coworkers on the electrodeposition of aluminium from hydride solutions. See also Refs.4 and 5.

§ Unfortunately obsolete terminology is often used (for example, in a review[7] which appeared after the present article had been sent to the press).

¶ The monomer AlH_3 and the dimer Al_2H_6 have been obtained in the gas phase at low pressure in the vaporisation of aluminium from a tungsten wire into a vacuum system with partly dissociated hydrogen[8].

† More stable ether addition compounds are known for the aluminium hydrohalides than for AlH_3, for example, $AlHCl_2.O(C_2H_5)_2$, and $AlHBr_2.O(C_2H_5)_2$.[13]

Table 1. Complexes of aluminium hydride.

System	Complex, production or method of detection	Properties
AlH_3-tetrahydrofuran	$AlH_3.2C_4H_8O$ *, 1) C_4H_8O vac. from soln. of AlH_3 in C_4H_8O at -45°C;[18] 2) Infrared[19] and NMR[16] spectra in soln. of AlH_3 in C_4H_8O.	stable at t_{room} only in soln. in C_4H_8O.[9] P_d = 6 mmHg, -5°C; 15 mmHg, +20°C.[18]
	$AlH_3.nC_4H_8O$, $n > 2$ not observed up to -65°C (tensimetric measurements)[18].	
	$AlH_3.C_4H_8O$, 1) C_4H_8O vac. from soln. of AlH_3 in C_4H_8O at t_{room}.[9,20] 2) 1 mole C_4H_8O vac. from $AlH_3.2C_4H_8O$ at -5°C.[18].	White cryst. subst., t_f = 56–57°C[16,20], sol. in e., THF, d., b., cyclohexane, iso-octane[16].
AlH_3-dioxan	$AlH_3.2OC_4H_8O$, $AlH_3.OC_4H_8O.C_4H_8O$, NMR[19] and infrared[9,16] spectra of soln. in d, and $AlH_3.OC_4H_8O$ in THF.	
	$AlH_3.OC_4H_8O$, OC_4H_8O vac. from soln. of AlH_3 in OC_4H_8O.[9,16]	white cryst. subst., does not melt, sol. in THF, d., insol. in b.[16].
AlH_3-trimethylamine	$AlH_3.2N(CH_3)_3$, 1) Treatment with amine of products of reaction in glow discharge: $Al(CH_3)_3 + nH_2 \rightarrow Al(CH_3)_{3-n}H_n + nCH_4$,[13] 2) $N(CH_3)_3 + (C_2H_5)_2O$ vac. from soln. AlH_3** and amine in e. at comp. ratio 1 : 2 or excess of amine[9,16,23,24]. Purification of subl.[23,25] or extr. b.[16]; 3) condensation of amine on $AlH_3.N(CH_3)_3$;[26] 4) tensim. titration of $AlH_3.N(C_2H_5)_3$ with gaseous $N(CH_3)_3$.[27].	white cryst. subst., t_f = 94–95°C[16,23], sol. in e., THF, b., cyclohexane, iso-octane[16,23]. Subl. impure subst., 30–40°C/1 mmHg[23] or at t_{room}.[24] At t_{room} stable in cryst. and in soln., dissoc. in gas[9,13,26,28] $AlH_3.2N(CH_3)_3 \rightleftarrows AlH_3.N(CH_3)_3 + N(CH_3)_3$.
	$AlH_3.N(CH_3)_3$*** 1) e. vac. from soln. AlH_3 and $N(CH_3)_3$ in e. at equimol. ratio of comp. or excess AlH_3. Purif. subl.[9,16,23] or extr.[9,16]. 2) Ruff's method[25,31] $LiAlH_4 + N(CH_3)_3.HCl \xrightarrow[t_{room}]{e.} AlH_3.N(CH_3)_3 + LiCl + H_2$, e. vac., subl. complex.	white cryst. subst., t_f = 74–76°C[16,23,26,29], sol. in e., THF, b., d., cyclohexane, iso-octane[16,23], P_d = 2–3 mmHg[26], subl. impure subst. 35–40°C, in vac.[26,31], 50–60°C, 1 mmHg.[23]
	$AlD_3.N(CH_3)_3$, Ruff's method[31], see above.	t_f = 77–78°C[31]
	$AlH_3.N(CH_3)_2CH_2CH{=}CH_2$, Ruff's method[31], see above.	t_f = 12°C[31]
AlH_3-dimethylamine	$AlH_3.2(CH_3)_2NH$, mixt. in e. AlH_3 with excess amine at -50°C, e. and excess amine vac. at -40°C[32].	at $t > -20$°C, chemical reaction: $AlH_3.2(CH_3)_2NH \rightarrow 2H_2 + AlH[N(CH_3)_2]_2$[32]
	$AlH_3.(CH_3)_2NH$, Ruff's method $LiAlH_4 + (CH_3)_2NH.HCl \xrightarrow[-40°C]{e.} H_2 + LiCl +$ $AlH_3.(CH_3)_2NH$[31]; assumed to be the same as preceding formation of $AlH_2N(CH_3)_2$.[32]	at $t > -10$°C, chem. reaction, see above[32].
AlH_3-methylamine	$AlH_3.2CH_3NH_2$, mixt. comp. in e. at -55°C at ratio 1 : 2 or excess of amine[33].	white solid, at $t > -40$°C, chem. reaction, $AlH_3.2CH_3NH_2 \rightarrow 2H_2 + HAl(NHCH_3)_2$.[33]
	$AlH_3.CH_3NH_2$, mixt. equimol. amount of comp. in e. at 55°C.[33].	white solid, at $t > -40$°C, chem. reaction, see above[33].
AlH_3-ammonia	$AlH_3.2NH_3$, proposed as preceding the formation of $H_2AlNH_2.NH_3$ at liq. nitrogen temp.[34]	at -80°C, chem. reaction $AlH_3.2NH_3 \rightarrow H_2 + H_2AlNH_2.NH_3$[34] at -45°C, chem. reaction, see above.[35]
	$AlH_3.NH_3$, mixt. equimol. amount comp. in e. at -80°C.[35]	
AlH_3-pyridine	$AlH_3.2C_5H_5N$, mixt. comp. in e. at -30°C to -40°C, e. and C_5H_5N vac.[36]	white cryst. subst., at 0°C, chem. reaction $AlH_3.2C_5H_5N \rightarrow HAl(NC_5H_6)_2$[36]
	$AlH_3.C_5H_5N$, mixt. comp. in e. at -30°C at equimol. ratio[36]	white cryst. subst., at t_{room}, chem. reaction, see above[36]
AlH_3-triethylamine	$AlH_3.N(C_2H_5)_3$: 1) e. vac. from equimol. soln. comp. in e.[16,36]. 2) Ruff's method[31] $LiAlH_4 + N(C_2H_5)_3.HCl \xrightarrow{e.} LiCl + H_2 + AlH_3.N(C_2H_5)_3$.	white cryst. subst.[36], t_f = 18–19.2°C,[31,36] melts readily supercools to -60°C,[36] subl. 0°C, high vac.[36], + 30°C/4.5 mmHg[36], sol. in e., b., triethylamine[16,36].
	$AlH_3.2N(C_2H_5)_3$ is not formed even in soln. of AlH_3 in $N(C_2H_5)_3$.[16,36]	
AlH_3-tripropylamine	$AlH_3.N(C_3H_7)_3$: 1) Ruff's method[31]: $LiAlH_4 + N(C_3H_7)_3.HCl \xrightarrow{e.}$ $LiCl + H_2 + AlH_3.N(C_3H_7)_3$; 2) mixt. comp. in e.[36]	white cryst. subst., t_f = 79.6–81.0°C,[27,29] sol. in e. and b.[36], subl. 30–40°C, in high vac.[36].
AlH_3-tributylamine	$AlH_3.N(C_4H_9)_3$, mixt. comp. in e.[36], purification only by recrystn. from b.[36]	t_f = 41.5°C, does not subl., decomp. into comp. at room temp.[36]
AlH_3-*NNN'N'*-tetramethylethylenediamine (L)	$AlH_3.L$: 1) Ruff's method: $LiAlH_4 + L.2HCl \xrightarrow[\text{excess}]{L} LiCl + H_2 + AlH_3.L$[37];	white solid, P_d = 1.5 mmHg, 99.3°C, 10.6 mmHg, 119.3°C, sol. in L[37].
	2) displacement of $N(CH_3)_3$ from the complex: $AlH_3.2N(CH_3)_3 + L \xrightarrow[\text{excess}]{L}$ $2N(CH_3)_3 + AlH_3.L$[37]	
AlH_3-*NNN'N'*-tetramethylpropanediamine ****(L)	$AlH_3.L$, displacement of $N(CH_3)_3$ from complex $AlH_3.N(CH_3)_3 + L \xrightarrow[\text{excess}]{L}$ $AlH_3.L + N(CH_3)_3$, purif. by subl.[10].	white solid, t_f = +140°C, subl. impure subst. 80°C, 0.05 mmHg[10].

* It was shown[21,22] by the isomolar series method (viscosity, density, electrical conductivity) that C_4H_8O forms complexes with $AlBr_3$ and $AlCl_3$, for example, in b. and $C_6H_5NO_2$ the complex $AlBr_3.C_4H_8O$.

** AlH_3 in e. obtained by $3LiAlH_4 + AlCl_3 \rightarrow 3LiCl + 4AlH_3$;[16,23] or $LiAlH_4 + HCl \rightarrow LiCl + H_2 + AlH_3$;[24] the polymer $(AlH_3)_x$, which dissolved in a soln. of $N(CH_3)_3$ in e.[9] was also used.

*** 1 : 1 adducts are known of $N(CH_3)_3$ with H_2AlCl, $HAlCl_2$, H_2AlBr, $HAlBr_2$;[29] aluminium alkyl hydrides also form complexes, for example, $CH_3AlH_2.N(CH_3)_3$, $(CH_3)_2AlH.N(CH_3)_3$.[30]

**** Complexes of AlH_3 with other polyamines are also obtained[10]; however, in these instances a chemical conversion is possible, which hinders the interpretation of the results. The complexes $AlH_3.L$ (L = triethylenediamine), stable up to > 200°C and insoluble in the usual organic solvents, were obtained[38] in tetrahydrofuran from Al, H_2, and L at moderate temperatures and hydrogen pressures.

Table 1‡ gives the methods of preparation and proof of the existence and also certain properties of the complexes of AlH_3. An appreciable proportion of the complexes exist only at low temperatures, above which a chemical reaction starts between the AlH_3 and the ligand.

Depending on the strength of the bonding of the ligands with AlH_3, some ligands can displace others to form more stable complexes, for example, NaH, LiH, and CaH_2 displace $N(CH_3)_3$ from its complexes with AlH_3[27] by reactions of the type:

$$LiH + AlH_3 \cdot N(CH_3)_3 \xrightarrow{(C_2H_5)_2O} LiAlH_4 + N(CH_3)_3 .$$

‡ In Tables 1 and 4 the following abbreviations and conventional symbols are used: vac. removal in a vacuum, soln. solution, subst. substance, sol. soluble, e. diethyl ether, THF tetrahydrofuran, d. dioxan, b. benzene, P_d dissociation pressure, comp. components, mixt. mixture, extr. extraction. The other symbols are understandable from the text.

NNN'N'-tetramethylethylenediamine (L) taken in excess, has a similar action[37]:

$$AlH_3 \cdot 2N(CH_3)_3 \xrightarrow[\text{solvent}]{L} AlH_3 \cdot L + 2N(CH_3)_3.$$

The same reactions take place with *NNN'N'*-tetramethylpropanediamine[10] and trimethylhydrazine[39].

By tensimetric titration of the complex $AlH_3.N(C_2H_5)_3$ with trimethylamine it was found that $N(CH_3)_3$ displaces $N(C_2H_5)_3$,[27] for $AlH_3.2N(CH_3)_3$ was isolated from the reaction mixture. NMR has shown[9] that C_4H_8O does not displace the amine from the complex $AlH_3.N(CH_3)_3$, and C_4H_8O in $AlH_3.C_4H_8O$ can be partly replaced by dioxan. The existence of the mixed complexes $AlH_3.N(CH_3)_3.C_4H_8O$, $AlH_3.N(CH_3)_3.OC_4H_8O$, and $AlH_3.C_4H_8O.OC_4H_8O$, has been found[16,19] in an excess of the complex-forming agent or solvent. The infrared spectra of solutions of $AlH_3.N(CH_3)_3$ in $N(C_2H_5)_3$, C_4H_8O, and OC_4H_8O showed[9] the presence of the compounds $AlH_3.N(CH_3)_3.N(C_2H_5)_3$, $AlH_3.N(CH_3)_3.C_4H_8O$, and $AlH_3.N(CH_3)_3.OC_4H_8O$, stable only in solution in an excess of the corresponding complex-forming substance. It is interesting that C_4H_8O and OC_4H_8O taken in excess give diadducts with AlH_3, but $N(C_2H_5)_3$ does not[9].

To explain the solubility of AlH_3 in diethyl ether, many authors propose the existence of the complexes $AlH_3.n(C_2H_5)_2O$, which were not isolated owing to their instability.

The precipitation of the ether-containing polymer $(AlH_3)_x$ from ethereal solutions of AlH_3, the stability of AlH_3 solutions in tetrahydrofuran and dioxan and of ethereal solutions of AlH_3 in the presence of LiBr or NR_3, and also the depolymerising action of tetrahydrofuran, tertiary amines, LiBr [3,9,16,36] on polymeric AlH_3 suggests that tetrahydrofuran, tertiary amines, and LiBr are stronger complex-forming agents than diethyl ether.

Accordingly, a series can be drawn up with the ligands arranged according to diminishing strength of the bond with AlH_3: alkali or alkaline earth metal hydrides > diamines > $N(CH_3)_3$ > OC_4H_8O, C_4H_8O, $N(C_2H_5)_3$ > $(C_2H_5)_2O$.

The ability of complexes to dissociate

$$AlH_3.L \rightleftharpoons AlH_3 + L$$

is also interesting. For the complexes of AlH_3 with alkali metal and alkaline earth metal hydrides such dissociation seems improbable although the decomposition

$$MAlH_4 \rightarrow MH + AlH_3$$

is proposed as a stage preceding certain chemical reactions[40] or the catalytic decomposition of $MAlH_4$ in ethereal solution[41,42].

Table 2 gives some information about the possibility of the dissociation in a vacuum

$$AlH_3.L \rightleftharpoons AlH_3 + L$$

of complexes with amines§.

The sequence of ligands according to the tendency of their complexes to dissociate from AlH_3 is: diamines < $< N(CH_3)_3 < N(C_2H_5)_3 < N(C_3H_7)_3 < N(C_4H_9)_3$. It should be noted that complexes with an odd number of carbon atoms in the alkyl radical of the amine melt at a higher temperature than those with an even number.

Depending on the ligand L and steric factors the complexes $AlH_3.L$ can add a second molecule of ligand ($AlH_3.L$ + + L ⇌ $AlH_3.2L$).

Quantitative data characterising this ability exist only for complexes with tertiary amines. The cryoscopic method was used[27] to measure the mean molecular weight of mixtures of NR_3 and $AlH_3.NR_3$, in benzene and the formation constants of the complexes, K, were calculated for certain amines: $AlH_3.2N(CH_3)_2CH_2CH{=}CH_2$, $K = 2 \times 10^2$; $AlH_3.2N(C_2H_5)_2CH_3$, $K = 3$; $AlH_3.2N(C_2H_5)_3$, $K = 8 \times 10^{-2}$. For $N(CH_3)_3$ the formation of the 1 : 2 complex is thought to be complete¶.

Table 2. Dissociation temperatures and melting points of the complexes $AlH_3.NR_3$.

Ligand	t_{dis}, °C	t_f, °C	References
$N(CH_3)_3$	100	75—76	20, 23, 27, 31
$N(C_2H_5)_3$	40 slow, 80 rapid	18—19.2	31.36
$N(C_3H_7)_3$	~40 in vacuum	79.6—81	31.36
$N(C_4H_9)_3$	readily dissociates in a vacuum, - does not distil	41.5	36
$N(CH_3)_2CH_2CH{=}CH_2$	—	12	31
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	does not dissociate at 133	—	37
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	does not dissociate at 140	136—140	10

Similar cryoscopic measurements were also made for the mixed complexes: $AlH_3.N(CH_3)_3.N(C_3H_7)_3$, $K = 7 \times 10^{-1}$; $AlH_3.N(CH_3)_3.N(C_2H_5)_3$, $K = 9$; $AlH_3.N(CH_3)_3.N(C_2H_5)_2CH_3$, $K = 5 \times 10^2$.

According to these results the stability order of the amino-complexes is: $N(CH_3)_3 > N(CH_3)_2CH_2CH{=}CH_2 > > N(C_2H_5)_2CH_3 > N(C_2H_5)_3 > N(C_3H_7)_3$. This series is also confirmed by qualitative results.

III. ALKALI METAL TETRAHYDROALUMINATES $MAlH_4$ AND THEIR COMPLEXES $MAlH_4.nL$

1. Methods of Preparation of $MAlH_4$

Rather effective methods for making alkali metal tetrahydroaluminates are now known, including the following which are suitable for industrial preparation:

(a) The reaction of the alkali metal hydride MH with $AlHal_3$ may be carried out in various solvents, the choice of which depends on the nature of M and Hal [12,15,41,43-53]. When MH is insoluble then the reaction proceeds in the presence of aluminium alkyls, the role of which reduces to the conversion of the MH into the soluble complexes $MAlHR_3$.[51,52] $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ are obtained in this way, and the reaction of LiH and $AlCl_3$ in $(C_2H_5)_2O$ serves for the industrial production of $LiAlH_4$.

It is thought[44,49,53] that the reaction of MH with $AlHal_3$ proceeds through the intermediate formation of AlH_3. The coordination unsaturated AlH_3 should, in our opinion, lead also to the formation of soluble complexes of composition

§ For other complexes the dissociation is complicated by the catalytic or thermal decomposition of AlH_3.

¶ This assumption is well based. The molecular weight of this complex in ether (ebullioscopy) and in benzene (cryoscopy) has been determined[8,16,26]. It has been shown that in both the compound is monomeric and not dissociated. The complex is completely stable in solution and in the crystalline form, whereas dissociation occurs in the gas

$$AlH_3.2N(CH_3)_3 \rightleftharpoons AlH_3.N(CH_3)_3 + N(CH_3)_3;$$

$$AlH_3.N(CH_3)_3 \rightarrow (AlH_3)_x + N(CH_3)_3.$$

as vapour pressure measurements and the infrared spectra have shown[9,26,28,37]. The polymers which are formed gradually break down into Al and H_2, that is, complete decomposition of $AlH_3.2N(CH_3)_3$ can proceed over a long time. The excess of $N(CH_3)_3$ shifts the equilibrium to the left.

$n MAlH_4.mAlH_3$. Evidently, at the start of the reaction $m \gg n$ and aluminium hydride predominates; at the end of reaction $m \ll n$ and $MAlH_4$ predominates in the solution. The decomposition of non-recrystallised $LiAlH_4$ usually observed is apparently connected above all with the decomposition of the impurity $MAlH_4.nAlH_3$. The hypothesis of the intermediate formation of the complex $LiAlH_4.AlH_3$ is made also for the reaction

$$3LiAlH_4 + AlCl_3 \rightarrow 3LiCl + 4AlH_3$$

from the results of NMR spectra [54].

(b) Direct reaction of the elements or MH, Al, and H_2 (the Al is specially activated [55-57]) on heating with hydrogen in solvating solvents [58-64], or hydrocarbons in the presence of aluminium alkyls and analogous compounds as activators [60,61,65]. In tetrahydrofuran and diglyme, Li, Na, and K tetrahydroaluminates have been obtained, in hydrocarbons, Na, K, and Cs.

In solvating media the direct preparation is complicated by cleavage of the solvent which at a definite temperature and concentration takes place explosively. Pyrophoric impurities are formed in the cleavage [58-61]. Solvent cleavage is intensified in the sequence Li–Cs, since $KAlH_4$ is obtained strongly contaminated and $CsAlH_4$ cannot be obtained at all in diglyme [60,61]. The explosive cleavage of diglyme by lithium tetrahydroaluminate [66] and of tetrahydrofuran by sodium tetrahydroaluminate [67] have been noted. The limiting temperatures for the coexistence of $LiAlH_4$ with diglyme, $NaAlH_4$ with C_4H_8O, and $NaAlH_4$ with diglyme are 200°, 165°, and 180°C respectively [60,61].

The vacuum distillation of the solvent after the preparation leads to contamination of the products from solutions of $MAlH_4$ in tetrahydrofuran and diglyme. On salting out the $MAlH_4$ from these solutions with ether or toluene, sufficiently pure $NaAlH_4$, $KAlH_4$, and $CsAlH_4$ are precipitated, but $LiAlH_4$ could not be isolated in this way.

In hydrocarbons, the direct preparation gives products with alkyl-substituted $MAlH_4$ as impurities, formed as a result of the reaction of aluminium alkyls with alkali metal hydrides.

The activating action of aluminium alkyls is explained by the formation of intermediate soluble complexes $MH.AlR_3$. [51,52,65] It has been suggested [56,58,65] that during the direct preparation of $MAlH_4$ there is the intermediate formation of AlH_3 from the elements, although this has been doubted [60,61], since the direct preparation of AlH_3 did not take place under conditions analogous to the direct preparation of tetrahydroaluminates [56]. Nevertheless without assuming the intermediate formation of AlH_3 or its subhydrides it is difficult to understand how the metallic aluminium is involved in the reaction.

It should be noted that the complex $AlH_3.L$ (L = triethylenediamine) has been prepared from Al, H_2, and L in tetrahydrofuran at moderate temperatures and hydrogen pressures [38].

In this reaction the formation of AlH_3 and polyhydroaluminates (or their partial alkyl derivatives) as a result of the hydrogenolysis of the compounds AlR_3 and $nMAlH_4.mAlR_3$ is quite probable [68,69]:

$$AlR_3 \xrightarrow{H_2} AlH_3 \xrightarrow{MH} MAlH_4;\ n\,MAlH_4 \cdot m\,AlR_3 \xrightarrow{H_2} n\,MAlH_4 \cdot m\,AlH_3.$$

Partly alkyl-substituted compounds give $MAlH_4$ as a result of the catalytic displacement of α-alkenes on heating [70,71].

From an analysis of the results on the direct preparation it can be concluded that the formation of $LiAlH_4$ from the elements is evidently determined ultimately by the magnitude of the solvation energy, which in tetrahydrofuran is sufficient for the formation of $LiAlH_4$. In diethyl ether and hydrocarbon solvents it is low and the change in free energy in the reaction [72]

$$LiH + Al + \tfrac{3}{2}H_2 \rightarrow LiAlH_4,\quad \Delta G = -3.9 \text{ kcal mole}^{-1}$$

is too insignificant to be the determining factor.

For sodium, potassium, and caesium tetrahydroaluminates the change in free energy is a significant quantity: for $NaAlH_4$ ΔG° = +3.0 kcal mole^{-1}, $KAlH_4$ ΔG° = +14.9 kcal mole^{-1}, $CsAlH_4$ ΔG° = +16.5 kcal mole^{-1}; [72] this also determines the possibility of their production in non-solvating media.

In the series $NaAlH_4$, $KAlH_4$, $CsAlH_4$ there is increasing solvent cleavage in their formation from the elements (125–150°C). The stability of the solvates should decrease in the same order (see below).

(c) Double decompositions of the type:

$$MAlH_4 + M'Hal \rightarrow M'AlH_4 + MHal\ [58,60,61,75]$$

and

$$M'AlH_4 + MH \rightarrow MAlH_4 + M'H\ [74],$$

the occurrence of which is determined by the ratios of the energies of formation of the reactants and final products and by solubility factors.

(d) Reactions for the replacement of an amine by a metal hydride [27]

$$AlH_3 \cdot NR_3 + MH \rightarrow MAlH_4 + NR_3.$$

Here the alkali metal hydride emerges as a stronger donor than the amine. The reaction

$$AlH_3 + MAlR_2H_2 \rightarrow MAlH_4 + R_2AlH,$$

where M = Na, K, has been proposed [65].

(e) The displacement

$$MAlH_4 + M' \rightarrow M'AlH_4 + M$$

where M = Li; M' = K, Rb, Cs [75].

2. Solubility and Complex Formation

The alkali metal tetrahydroaluminates are destroyed by water, ammonia, and other compounds with labile hydrogen. They are insoluble in non-polar solvents: benzene, toluene, aliphatic hydrocarbons. Table 3 gives the available information on solubility (m = moles per 1000 g solvent, c = moles per litre solution). In addition the solubility of $LiAlH_4$ is m = 1.1 in diethyl Carbitol [diethylene glycol diethyl ether] [12], m = 0.5 in dibutyl ether [12], m = 0.025 in dioxan [12], and $m > 1.5$ in methylal [80] (acetals are not reduced by $LiAlH_4$). A new solvent for lithium tetrahydroaluminate is "T-solvent"—tetrahydrofurfuroxytetrahydrofuran. The solubility of $LiAlH_4$ at 90°C is 22%. "T-solvent" boils at 238°C, which allows the reaction to be carried out at elevated temperatures [81].

$LiAlH_4$ is very slightly soluble in tertiary amines [12].

The great scatter in the results on the solubility of $LiAlH_4$ in diethyl ether is striking; it is due to the quality of the material dissolved [82]. Freshly prepared $LiAlH_4$ is more soluble in ether than the available commercial preparations [77]. The solubility of $MAlH_4$ is closely connected with the solvating ability of the solvents [58].

In several instances the solubility of tetrahydroaluminates can be compared with the properties of the complexes formed by $MAlH_4$ with the solvent. Table 4 gives the properties of the known complexes.

A series of complexes of the type $MAlH_4.nER_3$, where m = alkali metal and E = Al, Tl, In; R = alkyl; n = 1–4,

are also known; they were obtained by heating mixtures of the components[68]. The properties of most of these complexes have not been described, apart from $NaAlH_4.Al(C_2H_5)_3$, t_f = 60°C. It is also interesting to note the probable existence of $LiAlH_4.AlH_3$ [54] and $NaAlH_4.AlH_3$.[6]

Table 3. Comparison of the solubility of $MAlH_4$ in various solvents at room temperature.

Solvent	$MAlH_4$				
	$LiAlH_4$	$NaAlH_4$	$KAlH_4$	$CsAlH_4$	$Ca(AlH_4)_2$
Diethyl ether	m = 6.7-7.9[12] m = 6.7[17] m = 10.8[76] c = 7.9[77] c = 0.83[78]	insoluble[49,50**]			
Tetrahydrofuran	c = 3; 20°C[12]	c = 3; 20°[6,58]	poorly soluble[60,61] c = 0.03[58]		$c > 0.25$[6]
Monoglyme	c = 2.0; 20°C[58]	soluble[49]			
Diglyme	c = 1.0; 20°C[58]	c = 2,2; 20°C[58]	soluble[60,61]	soluble[60,61]	
Triglyme	c = 0.8; 20°C[58]	c = 2.8; 20°C[58]			
Tetraglyme	c = 1.8; 20°C[58]				

* The solubility was calculated by the authors[76] from the pressure-composition isotherm.

** $NaAlH_4$ is insoluble in $CH_3OC_2H_5$ and $CH_3OC_3H_7$.[49] The number of solvents for $NaAlH_4$ is limited to tetrahydrofuran and the methyl esters of mono- and poly-glycols.[79]

The instability of the complexes $MAlH_4.n(C_2H_5)_2O$ is illustrated by the solubility of only $LiAlH_4$ in $(C_2H_5)_2O$, the low heat of mixing of ether with $LiAlH_4$ (+1.95 kcal mole^{-1} [76]), and the ease of isolation of $LiAlH_4$ by simple vacuum distillation of ether from the solution.

The practical insolubility of $KAlH_4$, $RbAlH_4$, and $CsAlH_4$ in tetrahydrofuran, the relative ease of isolation of pure $NaAlH_4$ from C_4H_8O by salting-out with ether[58] or toluene[60] and the impossibility of this for $LiAlH_4$, and also the possibility of salting-out $KAlH_4$, $RbAlH_4$, and $CsAlH_4$ from their solutions in diglyme with toluene and the incompleteness of this for $LiAlH_4$ and $NaAlH_4$,[60] show the fall in stability of the solvates in the series $LiAlH_4 \rightarrow NaAlH_4 \rightarrow KAlH_4 \rightarrow RbAlH_4 \rightarrow CsAlH_4$. The essential role in solubility is evidently played not only by complex formation as such, but also the solvation of the alkali metal ions. In the series Cs, Rb, K, Na, Li the solvation of the ions by the ethers should increase. Moreover, it has been shown[93] that single complexes $[AlH_4.nL]^-$ are formed in C_4H_8O and diglyme, irrespective of M (see below). It should also be noted that although $LiAlH_4$ also forms comparatively stable complexes with dioxan and tertiary amines, it is practically insoluble in them[12]. In the strength of bonding of $LiAlH_4$ in the complex the ligands considered above can be arranged in the order:

$$(C_2H_5)_2O < C_4H_8O < OC_4H_8O \simeq NR_3.$$

From the point of view of the bond type and the possibility of existence of polyhydroaluminates, compounds with the general formula $MAlH_4.nAlR_3$, where R is an alkyl

Table 4. Complexes of the alkali metal tetrahydroaluminates.

System	Complex, production or method of observation	Properties
$LiAlH_4$–diethyl ether	$LiAlH_4.2(C_2H_5)_2O$ e. vac. from soln. of $LiAlH_4$ in e. at -60°C to constant weight[83].	$t_f \simeq$ -70°C, P_d = 38 mmHg, 0°C, readily sol. in e., loses e. even at t_{room}[83]
	$LiAlH_4.(C_2H_5)_2O$* (1) e. vac. from soln. of $LiAlH_4$ in e. at -15°C to const. weight[83]; 2) tensimetric measurements in the $LiAlH_4$–$(C_2H_5)_2O$ system[76,83].	e. light vac. (analogously at atm. pressure), being converted into $LiAlH_4$ on slight rise in t.[12,58,83] Isolation from e. on addition of b.[41,58,60] or hydrocarbons, which gives $LiAlH_4$ of higher purity than vac. e.[85]
$LiAlH_4$–tetrahydrofuran	$LiAlH_4.3C_4H_8O$, THF, vac. from soln. of $LiAlH_4$ in THF[16,83,86], for example, 17-20 mmHg, t_{room} or -20-0°C.[83]	colourless cryst. mass, t_f = 29-30°C[16,83,86], P_d = 16 mmHg, 0°C; 40 mmHg, 40°C[83]; sol. in e., THF, b.[83,86]; conc. soln. in e. forms layers, lower layer $LiAlH_4.3C_4H_8O$, upper satd. soln.[83].
	$LiAlH_4.2C_4H_8O$, tensimetric measurements during conversion of $LiAlH_4.3C_4H_8O$ into $LiAlH_4.C_4H_8O$;[83] 2) gas chromatography during addition of THF to soln. of $LiAlH_4$ in e.[87]	P_d = 15 mmHg, 34°C.[83]
	$LiAlH_4.C_4H_8O$, THF, vac. from soln. $LiAlH_4$ in THF 20-40°C[83,86], 40°C/3 mmHg.[16]	white solid, P_d = 1 mmHg, 20°C; 7 mmHg, 34°C[83]; readily sol. in e., THF, almost insol. in b.[16,83], last traces of THF difficult vac.[58,60].
$LiAlH_4$–trimethylamine	$LiAlH_4.3N(CH_3)_3$, mixt., comp. in e. at large excess of amine at -80°C.[88]	amine vac. even at -40°C, > 0°C converted into $LiAlH_4.N(CH_3)_3$.[88]
	$LiAlH_4.2N(CH_3)_3$, mixt. ethereal soln. of comp. at -50°C.[88]	white cryst. subst., in vac. at t_{room} converted into $LiAlH_4.N(CH_3)_3$.[88]
	$LiAlH_4.N(CH_3)_3$, mixt. ethereal soln. comp.[88]	white subst. sparingly sol. in e., insol. in b., decomposes in vac. at 180–200°C with separation of Al.[88]
$LiAlH_4$–triethylamine	$LiAlH_4.N(C_2H_5)_3$[89]	
$LiAlH_4$–triethylaluminium	$LiAlH_4.4Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	liq., $\kappa = 3.72 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.3Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	liq., $\kappa = 2.55 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.2Al(C_2H_5)_3$ Heating comp. at 80°C.[68,69]	t_f = 29°C, $\kappa = 1.46 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, 100°C.[69]
	$LiAlH_4.Al(C_2H_5)_3$ Heating at 100°C.[69]	solid, sol. in pet. ether[69], toluene[68]
$MAlH_4$–hydrides of tervalent elements	$MAlH_4.nEH_3$, n = 0.25-16, for example, $LiAlH_4.\frac{1}{2}AlH_3$, $NaAlH_4.\frac{1}{2}GaH_3$, $LiAlH_4.\frac{1}{2}InH_3$, $NaAlH_4.AlH_3$, $LiAlH_4.GaH_3$[90], combination of $MAlH_4$ in org. solvents, conductimetric and ebullioscopic measurements[90]. Series of substances isolated [from solution] by crystn. in vac.[90].	sol. in polar solvents (THF, e.)[90]
$NaAlH_4$–sodium hydride	$NaAlH_4.2NaH$, 1) $NaAlH_4 + 2NaH \rightarrow Na_3AlH_6$ in ball mill in heptane or xylene, 20–100°C; 2) $2Na + NaAlH_4 + H_2 \rightarrow Na_3AlH_6$; 3) $3Na + Al + 3H_2 \rightarrow Na_3AlH_6$, 150–160°C, H_2 pressure 180–110 atm[65,91].	solid, insol. in org. solvents[91].
$LiAlH_4$–lithium hydride	$LiAlH_4.2LiH$, $LiAlH_4 + 2C_4H_9Li \rightarrow Li_3AlH_6 + 3C_4H_8$ mixt. soln. C_4H_9Li in hexane with soln. $LiAlH_4$ in e. t_{room}[92].	solid, insol. in org. solvents, decomp. without fusion and sublimation 210°C.[92]

* The complex $NaAl(C_2H_5)_4.(C_2H_5)_2O$.[84]

radical or hydrogen, are extremely interesting. The complexes $MAlH_4.nAlR_3$, including $RbAlH_4.4Al(C_2H_5)_3$, have already been isolated and partly characterised[68]. It remains unclear whether the compounds $MAlH_4.nAlH_3$ are actually isolated in the pure state, or whether their existence is only surmised in solutions. It is curious that recently halogen analogues of the first member of the hydroaluminate series $LiAl_2H_7$ have been obtained: $LiAl_2Br_7$ and $LiAl_2I_7$.[94]

3. Some Reactions of Tetrahydroaluminates

For the electrochemistry of $MAlH_4$ it is essential to consider firstly those reactions which characterise the thermal and catalytic stability of $MAlH_4$, the capability of hydride hydrogen to be replaced, and solvent interaction.

Behaviour on heating. The thermal stability of lithium, sodium, and potassium tetrahydroaluminates increases in the order $LiAlH_4$–$NaAlH_4$–$KAlH_4$.[95-99] This suggests that $RbAlH_4$ and $CsAlH_4$ should have even greater thermal stability.

A peculiarity of the thermal decomposition of $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ is the stepwise evolution of hydrogen. Half the hydrogen is lost initially: $MAlH_4 \rightarrow MAlH_2 + H_2$. The temperature of this stage is: for $LiAlH_4$, 154–161°C[96] or 187–218°C[97]; for $NaAlH_4$, $> tf = 184$°C[97], for $KAlH_4$, 292–315°C[99]. The second stage corresponds to the decomposition $MAlH_2 \rightarrow MH + Al + \frac{1}{2}H_2$ and its temperature is: for $LiAlH_4$, 197–227°C[96], or 228–282°C[97]; for $NaAlH_4$ 290–298°C[98]; and for $KAlH_4$, 335–365°C[99]. The remaining hydrogen is lost by decomposition of the alkali metal hydride: $MH \rightarrow M + \frac{1}{2}H_2$, which corresponds to the temperatures: for $LiAlH_4$ 580–586°C[96], or 370–483°C[97], for $NaAlH_4$ 422–432°C[98], and for $KAlH_4$ 425–430°C[99]. The scatter of the results for lithium hydroaluminates is probably due to a difference in the purity of the substances tested.

Mikheeva and coworkers consider that all the stages of the decomposition of $LiAlH_4$ are endothermic[96]. However others[97] have found that the first stage of the decomposition (to $LiAlH_2$) is exothermic. The latter agrees with the thermochemical results. The decomposition of $LiAlH_4$ to LiH is exothermic, which is contrary to the behaviour of the other hydroaluminates[72]. All stages of the decomposition of $NaAlH_4$ and $KAlH_4$ are exothermic. $NaAlH_4$ melts almost without decomposition.

We note also that a reversible phase transformation of unknown nature has been found[97] for $LiAlH_4$ in the range 160–177°C.

Catalytic decomposition of $LiAlH_4$. In accordance with the decrease in free energy in the decomposition $LiAlH_4 \rightarrow LiH + Al + \frac{3}{2}H_2$,[72] $LiAlH_4$ is metastable, in contrast with sodium, potassium, and caesium tetrahydroaluminates. Solid preparations of $LiAlH_4$ darken on long storage, especially in the light, and gradually decompose, especially in the presence of catalytic additions of Ti, Si, Fe, Cu, or B[41]. When aluminium powder is dusted into an ethereal solution of $LiAlH_4$ the latter decomposes violently[58]. Highly disperse aluminium formed in the decomposition of solid $LiAlH_4$ is evidently the cause of the self-acceleration of the process. The decomposition of $LiAlH_4$ has been connected[100] with the initial homolytic splitting of $LiAlH_4$ into LiH and AlH_3. However, we think it much more probable that the initiation of the decomposition of the preparations is connected with the instability of the complexes $LiAlH_4.nAlH_3$ present as impurities (see p. 101/102).

This suggestion fits in well with the fact that the stabilisation of solid preparations of $LiAlH_4$ involves removal of the impurities as much as possible. This is done by dissolution of the preparations in $(C_2H_5)_2O$ and long boiling[100], especially in the presence of LiH[42], and also by bonding the impurities in complexes by the addition (up to 6%) of dioxan, dimethylcellosolve, and trimethylamine[101]. The complexes formed with AlH_3 are capable of regenerating $LiAlH_4$ in ethereal solution in the presence of lithium hydride[42]:

$$AlH_3 \cdot L + LiH \rightarrow LiAlH_4 + L.$$

A stabilising action on $LiAlH_4$ due to complex formation is shown by tetrahydrofuran and diglyme, which form completely stable solutions with $LiAlH_4$ at room temperature[58,60]. Here the stability of the solvates of $LiAlH_4$ is so great that it cannot be freed from solvent (see p. 102/103).

Reaction of $MAlH_4$ with solvents. Alkali metal hydroaluminates are not completely inert to solvents, especially on heating (see p. 102).

Explosive reactions of $LiAlH_4$ with dimethyl ether[102] and perfluorosuccinamide[103] have been noted, in addition to the splitting of tetrahydrofuran, dioxan, diethoxyethane, and dibutyl ether by a mixture of $LiAlH_4$ and $AlCl_3$.[104,105] Information about the splitting of $(C_2H_5)_2O$ by lithium tetrahydroaluminate is not available.

IV. STRUCTURE OF THE COMPLEXES $AlH_3.nL$ AND $MAlH_4.nL$

The complexes of AlH_3 have been better studied than the complexes of the alkali metal tetrahydroaluminates and for $n = 1$, 2 and various L they are known in all states of aggregation. The most reliable and confidently interpreted results were obtained for the gaseous complexes with $N(CH_3)_3$. At $n = 1$ the infrared spectra show the tetrahedral configuration of the molecules of the complex with symmetry C_{3v}.[9,26,106] In this sense they are similar to the anions formed in the aluminium compounds of type $MAlR_4$, where R is halogen or alkyl[3,107-109]. The anion AlH_4^- in $MAlH_4$ also exhibits an analogous structure[77,93,110] with an Al–H distance between 1.61[111] and 1.66 Å,[112] a conclusion reached on the basis of an investigation of the infrared and Raman spectra in ether[77,110] and in the solid state[77]. The valence state of the aluminium atom in such compounds corresponds to sp^3 hybridisation[20,113]. For other compounds of aluminium hydride in which the aluminium has coordination number four such definite conclusions cannot be drawn owing to the absence of corresponding experimental data: not one of them apart from $AlH_3.N(CH_3)_3$ has been studied in the gas phase and only two—$AlH_3.C_4H_8O$ and $AlH_3.N(C_2H_5)_3$ have been studied in inert solvents[9,16,20,114,115]. In the last examples the considerable similarity between these spectra and the spectra of solutions of the complex $AlH_3.N(CH_3)_3$ in the same solvent suggests that the molecules of these complexes have analogous structure[20].

For the complex $AlH_3.2N(CH_3)_3$ information is available about the infrared spectra in the gas[9,26,106] and in inert solvents[16,20,114,115], the Raman spectra of solutions[26,106], and the structure of crystals[24]. These results show definitely that the molecule of the complex is a trigonal bipyramid with three H atoms in the base [sic], an Al–N distance of 2.18 Å and an N–Al–N angle of 180°. Such a

structure corresponds to sp^2-pd hybridisation (three planar sp^2-bonds and two pd-orbitals perpendicular to their plane)[19,20,27], symmetry group D_{3h} [20,26,106] or D_3.[106] From the similarity of the spectra of solutions of AlH_3 in complex-forming solvents and by general analogy such a structure can also be suggested for complexes with $2C_4H_8O$, $2OC_4H_8O$, and the mixed compound $AlH_3.C_4H_8O.OC_4H_8O$.[16]

At the same time some uncertainties about the frequencies still exist even for the complexes with $N(CH_3)_3$. The Al–N stretching vibration in compounds of the 1 : 1 type has been assigned the frequency 533 cm^{-1} on the grounds that it is unchanged on going to $AlD_3.N(CH_3)_3$, whereas all the others show a decrease in frequency of a factor of $\sqrt{2}$.[26] However, the absorption in this region is very weak so that Roszinski and Dautel[9] could not even detect it in deuteriation. This fact is puzzling.

In the 1 : 2 complexes the N–Al–N symmetric stretching vibrations are from the same considerations assigned the frequency 461 cm^{-1} (Raman spectra, inactive in the infrared spectrum) and the asymmetric, 460 cm^{-1} (infrared spectrum, inactive in the Raman spectrum)[26], 466 cm^{-1}, and 460 cm^{-1}.[106] The proximity of these values is strange, since the light aluminium atom takes part in the asymmetric vibrations, and consequently the shift should be more pronounced. This contradiction has been explained[106] by the spectra's being obtained under different conditions—the infrared spectrum in the gas, and the Raman spectrum in $N(CH_3)_3$ as solvent. An attempt has been made[116] to calculate the frequency of the corresponding vibrations theoretically; however, by making a series of necessary assumptions the authors did not obtain values which agree well with those observable experimentally. They all concluded that the frequency of the symmetric vibrations should be found in the 150–200 cm^{-1} region. Actually, in the Raman spectrum absorption is observed[106] at 197 cm^{-1}, which the authors[106] assigned to the deformation vibrations of the Al–N bond and two absorption bands at 142 and 114 cm^{-1}, not assigned to any vibrations owing to the absence of an absorption spectrum for $N(CH_3)_3$ in this frequency range. In fact, one of them could be a deformation vibration since it is known that the N–Al–N bond is very readily deformed[24,106]. Evidently, further investigation is necessary.

In the complexes with tetrahydrofuran and dioxan the position is still more uncertain. The stretching vibration of the Al–O bond in $AlH_3.C_4H_8O$ was assigned the frequency 538 cm^{-1} in benzene solution, by analogy with the corresponding frequency in the complex with $N(CH_3)_3$.[9] However, in the spectra of solutions of AlH_3 in $AlH_3.N(CH_3)_3$ in tetrahydrofuran frequencies above 400 cm^{-1} which could be assigned to the Al–O or Al–N vibrations are not observed[9,16]. On the contrary, the frequency 455 cm^{-1}, provisionally assigned to the Al–O stretching vibrations is observed in the spectra of these substances and of $AlH_3.C_4H_8O$ in dioxan and of $AlH_3.OC_4H_8O$ in tetrahydrofuran[9]. There are, however, grounds for assuming that it is due to the deformation vibrations of the dioxan ring, inactive in the infrared spectrum in pure dioxan and which appears on destroying its symmetry by interaction with AlH_3.[16] Precise determination of the vibration frequencies of the aluminium–donor atom bond would be extremely desirable to solve problems connected with the stability of the complexes.

In this respect the dependence of the stretching frequencies of AlH_3 on the strength of the ligand–aluminium bond is interesting. Zeil and coworkers[20], having comparatively meagre data at their disposal, evaluated the force constant of this bond and found that it decreases in the series of compounds $AlH_3 > AlH_4^- > AlH_3.C_4H_8O > AlH_3.2N(CH_3)_3$. Schomburg and Hoffman[115] compared the displacement of the Al–H vibration frequency with the heat of reaction of AlH_3 with various ligands[117] and observed that they were symbathic. Later this relation was used repeatedly, was generalised, and was taken as a general rule[9,16,114]. However, the conclusions given in the literature need to be reconsidered, since they were obtained by comparing spectra for different states of aggregation and using spectra of crystalline substance, which is scarcely permissible in the absence of reliable assignment of frequencies and clear information about the character of the interaction of the molecules of the complexes in the crystalline state. Table 5 gives the stretching vibration frequencies of the Al–H bond from the spectra obtained under comparable conditions. The concentration of the test solutions is not always given in the original studies, but as far as can be judged in all the instances quoted it does not exceed 0.5 M. The observed difference between the various data are evidently explained by the experimental difficulties with such active substances.

Table 5 suggests that the ligands can be arranged according to the strength of the bond with aluminium in the 1 : 1 complexes in the series: $N(CH_3)_3 > C_4H_8O > N(C_2H_5)_3$. It is also evident that the solvents concerned are sufficiently inert in relation to these complexes, since the frequency

Table 5. Stretching vibrations of the Al–H bond in dilute solutions of the complexes AlH_3L in inert solvents at room temperature, cm^{-1}.

Complex	Solvent	Stretching vibration	Reference	Complex	Solvent	Stretching vibration	Reference
$AlH_3.N(C_2H_5)_3$	C_6H_5	1778	16	$AlH_3.N(CH_3)_3$*	C_6H_6	1778	16
	C_6H_{12}	1779	115		C_6H_{12}	1786	16
		mean 1778			C_6H_{18}	1786	16
$AlH_3.C_4H_8O$	C_6H_6	1778	16		C_6H_6	1786	114
	C_6H_{18}	1786	16		C_6H_{12}	1788	115
	C_6H_6	1786	114		C_6H_6	1803	315
	C_6H_{12}	1794	16			mean 1787	
		mean 1786					

* In the gaseous state: 1792 cm^{-1}.[26]

in the gas and in them are very close. The latter relates also to $AlH_3.2N(CH_3)_3$, the only non-mixed 1 : 2 complex, studied in inert solvents: 1706 (C_6H_{12} [115]), 1702 (C_6H_6 [16]), and 1690 (C_6H_6 [114]) (mean 1700) and 1709,[26] 1709,[9] and 1711 cm^{-1} [106] (mean 1710 cm^{-1}) in the gas. For the remaining complexes, which contain more than one ligand molecule per AlH_3 molecule, information exists only for their solutions in the same ligand (Table 6) or in another (Table 7). In all these instances the frequency relates to the Al–H asymmetric stretching vibrations, since they are obtained from the infrared spectra, in which the symmetric vibrations are inactive.

To draw the correct conclusions from Table 6 it is necessary to bear in mind two additional circumstances. Firstly, a second $N(C_2H_5)_3$ molecule is not added even in a solution of AlH_3 in this substance[9,16,26]. Secondly, $(C_2H_5)_2O$ exhibits some anomalies in comparison with other ligands, namely, in benzene solution, with AlH_3 and $(C_2H_5)_2O$ in the ratio 1 : 4, absorption is observed at 1840 cm^{-1}, and at 1800 cm^{-1} there is only a "shoulder". Evidently this must be understood as an indication that in a solution of AlH_3 in

$(C_2H_5)_2O$ a 1 : 2 complex is formed, which in benzene is largely decomposed into the 1 : 1 complex and free $(C_2H_5)_2O$. True, it has been suggested[16] that at coordination number 5 the Al–H frequency should be $\geqslant$ 1750 cm^{-1}, but probably the anomaly once again consists in a departure from this rule, which holds well for other ligands. When this observation is taken into account, then according to Table 6 we obtain the following series of strengths of the bond between the ligands and aluminium hydride in the 1 : 2 L complexes: $N(CH_3)_3 > C_4H_8O > OC_4H_8O > (C_2H_5)_2O > N(C_2H_5)_3$.

This conclusion is confirmed in the NMR spectra for AlH_3 in the 1 : 1 and 1 : 2 complexes with $N(CH_3)_3$ and C_4H_8O, the chemical shift in which is greater for $N(CH_3)_3$.[19]

Table 6. Stretching vibrations of the Al–H bond in solutions of the complexes $AlH_3.L$ in corresponding solvents L, cm^{-1}.

Complex	Stretching vibration	Reference	Complex	Stretching vibration	Reference
$AlH_3 \cdot N(CH_3)_3$	1710	26	$AlH_3 \cdot OC_4H_8O$	1754	16
$AlH_3 \cdot C_4H_8O$	1724	114	$AlH_3 \cdot N(C_2H_5)_3$	1778	16
$AlH_3 \cdot C_4H_8O$	1739	16	$AlH_3 \cdot (C_2H_5)_2O$	1801	114

Table 7. Stretching vibrations of the Al–H bond in solutions of the complexes $AlH_3.L$ in complex-forming solvents L', cm^{-1}.

Complex	Solvent	Stretching vibration	Reference	Complex	Solvent	Stretching vibration	Reference
$AlH_3 \cdot LiH$	C_4H_8H	1674	16	$AlH_3 \cdot N(CH_3)_3$	C_4H_8O	1710	114
$AlH_3 \cdot LiH$	C_4H_8O	1678	93	$AlH_3 \cdot N(CH_3)_3$	C_4H_8O	1724	16
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1733	77			mean 1717	
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1740	110	$AlH_3 \cdot N(CH_3)_3$	$(C_2H_5)_2O$	1724	114
$AlH_3 \cdot LiH$	$(C_2H_5)_2O$	1746	118	$AlH_3 \cdot N(CH_3)_3$	OC_4H_8O	1732	16
		mean 1740		$AlH_3 \cdot N(C_2H_5)_3$	C_4H_8O	1740	115
				$AlH_3 \cdot C_4H_8O$	OC_4H_8O	1747	16
				$AlH_3 \cdot OC_4H_8O$	C_4H_8O	1747	16

For the formation of 1 : 2 mixed complexes of type $AlH_3.L.L'$ the position is more complex. It is evident directly from Table 7 that in the addition of various ligands to $AlH_3.N(CH_3)_3$ the compounds which are formed are arranged in the following series according to stability: $C_4H_8O > (C_2H_5)_2O > OC_4H_8O$, where OC_4H_8O and $(C_2H_5)_2O$ change places in comparison with the 1 : 2L complexes. The same order for C_4H_8O and $(C_2H_5)_2O$ is kept also in their addition to $AlH_3.LiH$.

On the basis of the results collected in Tables 5–7 and those on a solution of $AlH_3.C_4H_8O.(C_2H_5)_2O$ in C_6H_6,[114] it can be shown that the shift in the Al–H frequency on the addition of L' to $AlH_3.L$ depends on the nature of L and L', despite conclusions[16] drawn from a comparison of spectra obtained under poorly comparable conditions (Table 8). For comparison, Table 8 also gives the displacement in the formation of complexes of type $AlH_3.2L$. The NMR spectra also confirm that the addition of the second C_4H_8O molecule to $AlH_3.C_4H_8O$ is less favourable than that of $N(CH_3)_3$ to $AlH_3.N(CH_3)_3$.[19] Unfortunately, on account of the absence of information under comparable conditions the shift in frequency during the formation of AlH_4^- from AlH_3 cannot be determined. However, reliable estimates using the results on solutions of $LiAlH_4$ in C_4H_8O and $(C_2H_5)_2O$ show that it lies within the limits 60–100 cm^{-1}, that is, almost equal to the shift brought about by the most strongly bound ligands. The values found for $\Delta\nu$ agree with the facts that $N(CH_3)_3$ is not displaced from the complexes by tetrahydrofuran and dioxan, whereas in an excess of OC_4H_8O the C_4H_8O is partly replaced with the formation of $AlH_3.2OC_4H_8O$.[19] At the same time it should be noted that the symbathic relation between $\Delta\nu$ and the tendency for complex formation is absent. Thus the addition of the first $N(C_2H_5)_3$ molecule brings about almost the same displacement as the addition of $N(CH_3)_3$; however, in the first instance the 1 : 2 compound is not formed completely, whereas in the second it is formed and seems completely stable. Further, the compounds with $2C_4H_8O$ and $2OC_4H_8O$ are formed only in an excess of the ligands[9], but the addition of $(C_2H_5)_2O$ to $AlH_3.N(CH_3)_3$, even in $(C_2H_5)_2O$ takes place only partially despite the high value of $\Delta\nu$. This is so because the absorption at 1724 cm^{-1}, which corresponds to the complex $AlH_3.N(CH_3)_3.(C_2H_5)_2O$, is very weak and the strong absorption corresponding to the $AlH_3.N(CH_3)_3$ molecules is retained[114]. In the literature these facts are attributed to steric hindrance[9,114], but no additional confirmation of this has yet been found. It therefore remains uncertain what aspect of the steric factors are significantly less favourable for $N(C_2H_5)_3$ than for $(C_2H_5)_2O$ or C_4H_8O and OC_4H_8O. The uncertainty is even further aggravated by the fact that the rather stable compounds $AlH_3.2NCH_3(C_2H_5)_2$ and $AlH_3.N(CH_3)_3.N(C_2H_5)_3$ are formed[27].

From the results of Tables 6 and 7, clearly in an excess of ligand the compounds $AlH_3.L$ (L $\neq$ LiH) do not give complexes with $n > 2$. From Table 8 it follows that the most favourable formation of mixed complexes occurs at L = $N(CH_3)_3$. At the same time, according to Ehrlich and coworkers[114] the vibrations of the Al–H bond for solutions of $AlH_3.2N(CH_3)_3$ in C_4H_8O—the strongest ligand after $N(CH_3)_3$—and in $(C_2H_5)_2O$ lie at 1695 cm^{-1} and the same vibrations for solutions of $AlH_3.2N(CH_3)_3$ in benzene, at 1690 cm^{-1}. Hence, clearly, complexes with a coordination number 6

Table 8. Displacement of the frequencies of the Al–H stretching vibrations on going from $AlH_3.L$ to $AlH_3.L.L'$.

L*	L'	Condition of production of spectrum of $AlH_3.L.L'$	$\Delta\nu$, cm^{-1}	L	L'	Condition of production of spectrum of $AlH_3.L$	Condition of production of spectrum of $AlH_3.L.L'$	$\Delta\nu$, cm^{-1}
$N(CH_3)_3$	C_4H_8O	soln. in C_4H_8O	70	$N(CH_3)_3$	$N(CH_3)_3$	inert solvent	soln. in C_6H_6	88
$N(C_2H_5)_3$	C_4H_8O	soln. in C_4H_8O	38	C_4H_8O	C_4H_8O	inert solvent	soln. in C_4H_8O	54
$N(CH_3)_3$	OC_4H_8O	soln. in OC_4H_8O	55					
C_4H_8O	OC_4H_8O	soln. in OC_4H_8O	39					
C_4H_8O	$(C_2H_5)_2O$	soln. in C_6H_6	76	$(C_2H_5)_2O$	$(C_2H_5)_2O$	soln. in $(C_6H_6)+(C_2H_5)_2O$	soln. in $(C_2H_5)_2O$	40
$N(CH_3)_3$	$(C_2H_5)_2O$	soln. in $(C_2H_5)_2O$	63					

* All the spectra of $AlH_3.L$ were obtained in inert solvents.

for aluminium are not formed in such mixtures. However, $\nu_{Al-H}LiAlH_4$ in C_4H_8O (Table 7) and the liquid mixture $AlH_3.LiH : C_4H_8O = 1:8$ lies at 1674 cm^{-1}, but in a solution of the mixture $AlH_3.LiH : C_4H_8O = 1:3$ in benzene, at 1724 cm^{-1}.[16] Hence the conclusion (which should be confirmed by a more thorough and detailed investigation) that instances of complex formation in the liquid phase with a coordination number of 6 for Al are clearly possible. This is suggested, in particular, by the infrared spectra of solutions of the alkali metal tetrahydroaluminates, $CsAlH_4$–$LiAlH_4$, in diglyme and of $LiAlH_4$ and $NaAlH_4$ in C_4H_8O.[93] It was found[92] that the spectra agree with the existence of the anion $[AlH_4.2L]^-$. However, they can be interpreted also without this assumption, which needs additional proof.

The next question, directly connected with the stability of the complexes formed, is the change in the state of ligand molecules on coordination with Al. Unfortunately, little information is available here. Of the 1:1 complexes only that with $N(CH_3)_3$, and of the 1:2 complexes those with $N(CH_3)_3$ and C_4H_8O, have been investigated. In $AlH_3.N(CH_3)_3$ a shift in the N–C stretching frequency in the $N(CH_3)_3$ molecule from 1040 cm^{-1} in pure $N(CH_3)_3$ (gas) to 1005 cm^{-1} in complexes (gas)[26] or 1000 cm^{-1} (solution in C_6H_6)[16] is observed. In the solutions of the complex in C_4H_8O and OC_4H_8O this frequency lies at 1018 and 1015 cm^{-1} respectively[16]. The 997–1002 cm^{-1} absorption band was also observed in the liquid 1:1 complexes of $N(CH_3)_3$ with $(C_2H_5)_2AlH$, $(C_2H_5)AlH_2$, $(CH_3)_2AlH$, and CH_3AlH_2.[30] For the 1:2 compounds with $N(CH_3)_3$ the results are less unequivocal: Heitsch and Kniselly[106] did not observe a change in the infrared spectrum of $N(CH_3)_3$ in the gaseous complex, and Dautel and Zeil[16] observed an absorption band at 1015 cm^{-1} in the benzene solution of the complex. They did not observe[19] a chemical shift of the NMR lines for the protons of the CH_3 groups. Evidently these results suggest a comparatively weak change in the state of the $N(CH_3)_3$ molecules. This can be explained by the free electron pair of the nitrogen in $N(CH_3)_3$ already participating in the sp^3-hybridisation of this atom (the angles of the C–N–C bonds are close to tetrahedral)[19]. On the other hand, in the $AlH_3.2C_4H_8O$ complexes a drop in the resonance frequency in the NMR spectrum of the proton in the α-CH_3 group by 10 Hz is observed, whereas in the β-CH_2 groups there is no chemical shift. This is explained by the strong change in the valence state of the O atom, the [bonding] eigenfunction of which in the free ligand is the p-function (possibly, with a small fraction of s-character)[19]. It is quite probable that the change in energy level of the molecule of the ligands plays a considerable part of the role which is ascribed to steric hindrance in the attempts to explain the observed regularities in complex formation.

Generally speaking, the structure of the complexes considered above in the condensed state can undergo definite changes owing to association if this involves a change in the coordination number of aluminium or the setting up of ligand–ligand bonds. Table 9 gives results on the degree of association of several complexes. The possibility of the formation of bonds between these ligands, already coordinated with aluminium, is almost absent. Consequently, the association can be due either to the high values of the dipole moments ($\mu \simeq 3$–5 D[26,115,118]) or the formation of hydrogen bridges, the possibility of which for solid AlH_3 was first shown by Longuet-Higgins[119]. Subsequently this idea was extended by other authors to solutions of its complexes. Let us first consider the liquid state.

The formation of hydrogen bridges should be indicated in the infrared spectra by: (1) broadening of the bands for the Al–H stretching vibration, (2) the shift to lower frequencies of this vibration, and (3) the appearance of certain new lines in the spectrum. In the NMR spectra there should be corresponding displacements. Not one of these phenomena occurs in the solutions in inert solvents, at least up to 0.5 M concentration[19,20,26,31,77,115]. Moreover, Wiberg and coworkers[25] found that at the b.p. of solutions of $LiAlH_4$ in diethyl ether the molecular weight of $LiAlH_4$ increases with concentration and corresponds to $(LiAlH_4)_2$ at 0.08 M, and to $(LiAlH_4)_3$ at 0.8 M, which they explain by the formation of hydrogen bridges, However, a change in the form and a displacement of the absorption bands of the complex up to 3.4 M was not observed in the infrared and Raman spectra[77,110] of these solutions although the degree of association is sufficiently high even in dilute solutions (cryoscopy, Table 9), and a concentration of 0.3–0.5 M is completely sufficient for obtaining clear spectral data. The association of hydrides of the type R_2AlH has been investigated by cryoscopic methods and by infrared and Raman spectroscopy[118,120]. It was found that in the liquid state, dilute solutions, inert solvents, and in the gas these compounds are trimers owing to the formation of hydrogen bridges with aluminium in coordination number 4. Very strong absorption bands for the Al–H of the trimers lie in the 1770 cm^{-1} range and have a half-width of $\sim$ 100 cm^{-1} (concentration of solutions $\sim$ 0.1 M). The addition of strong complex-forming ligands, such as $N(CH_3)_3$, C_4H_8O, and $(C_2H_5)_2O$ leads to the breakdown of the trimers and the formation of 1:1 complexes with the aluminium coordination number remaining at four, this being accompanied by a marked narrowing of the absorption bands and their displacement to lower or higher frequencies (see also Schomburg and Hoffman[115]), depending on the ligand. The latter is understandable, since here there are two effects superimposed—displacement to higher frequencies on breaking the hydrogen bridge, and to lower during coordination of the ligand. However, no narrowing of the absorption bands takes place during the formation of the complexes $AlH_3.2L$ or $AlH_3.L.L'$ from $AlH_3.L$.[9,14] Further, in the addition of L' to $AlH_3.L$ the maximum displacement of frequency to the side of lower frequencies takes place for $L = N(CH_3)_3$ (Table 8), that is, when α is

Table 9. Degree of association α of the complexes from cryoscopic results.

Complex	Solvent	Concentration, M	α	Reference
$AlH_3 \cdot N(CH_3)_3$	C_6H_6	0.13—0.61	1.40—1.44	23, 25, 31, 114
$AlH_3 \cdot C_4H_8O$	C_6H_6		1.55	114
$AlH_3 \cdot (C_2H_5)_2O$	C_6H_6		1.21	114
$AlH_3 \cdot N(CH_3)_2CH_2CH{=}CH_2$	C_6H_6		1.37	31
$AlH_3 \cdot NCH_3(C_2H_5)_2$	C_6H_6	0.48—0.78	1.33	31
			1.10	31*
$AlH_3 \cdot N(C_2H_5)_3$	C_6H_6	0.19—0.39	1.57	23,25
$AlH_3 \cdot N(C_3H_7)_3$	C_6H_6	0.30—0.57	1.05	31
$AlH_3 \cdot N(C_4H_9)_3$	C_6H_6		1.17	23,25
$CH_3AlH_2 \cdot N(CH_3)_3$	C_6H_{12}		1.95	30
$(CH_3)_2AlH \cdot N(CH_3)_3$	C_6H_{12}		1.34	30
$C_2H_5AlH_2 \cdot N(CH_3)_3$	C_6H_{12}		1.60	30
$(C_2H_5)_2AlH \cdot N(CH_3)_3$	C_6H_{12}		1.18	30
$AlD_3 \cdot N(CH_3)_3$	C_6H_6		1.43	31
$AlH_3 \cdot 2N(CH_3)_3$	C_6H_6		1	9, 16, 26

* The authors[31] found it difficult to explain this departure from Wiberg's results[23,25].

highest (Table 9) and a significant difference in sign of the contribution from the breaking of the hydrogen bridges would be expected. Hydrogen bridges are absent from a solution of AlH_3 in diethyl ether, in which AlH_3 is monomeric[12] although the bonding of AlH_3 in ether is weak. Probably the $(C_2H_5)_2O \rightarrow AlH_3$ donor–acceptor bond, in decreasing the formal positive change on Al, leads to loss by the AlH_3 molecule of the ability to give hydrogen bridges. It therefore seems improbable that bridges can be formed by AlH_3 molecules bound with such strong donors as amines.

Ruff[29], in considering the results of Ulich and Nespital[121] for solutions of complexes of aluminium halides, also considers that the association of these complexes is more similar to the dipole–dipole interaction than to polymerisation through halogen bridges.

The dipole–dipole interaction hypothesis accords with symmetric $AlH_3.2N(CH_3)_3$, the dipole moment of which is close to zero, not being associated in benzene (Table 9), although the coordination number of aluminium does not have the maximal value of 6 (see Refs. 9, 13, 119, 122).

The association of $AlH_3.NR_3$ in benzene decreases with increase in the length of the amine radical (Table 9)[23,25,31]. Such a relation contradicts the hypothesis of hydrogen bridge formation, since with decrease in the radical length the stability of the complexes of AlH_3 with NR_3 increases, corresponding to a decrease in the effective positive charge on the Al in the $Al^{\delta+}-H^{\delta-}$ bond[19], which should hinder the formation of hydrogen bridges, that is, decrease the degree of association.

The main argument supporting the existence of hydrogen bonds in benzene solutions is thought[23,25,31] to be the association of $AlH_3.NR_3$, in contrast with the monomeric nature of $AlH_3.NR_3$ in diethyl ether. This, in the opinion of the authors, is connected with the breaking of hydrogen bonds due to donor–acceptor interaction with ether. However, the monomeric nature can be explained also by inhibition of the dipole–dipole interaction of the $AlH_3.NR_3$ molecules in diethyl ether, because of the somewhat greater dielectric constant of ether in comparison with benzene, and also the weakening due to the decrease in μ of the complex, since in an excess of ether unstable mixed diadducts can be formed, $AlH_3.NR_3.(C_2H_5)_2O$ with $\mu \simeq 0$.

The absence of association (according to ebullioscopic results[88]) of $LiAlH_4$ in C_4H_8O can be explained in a similar manner.

Hence if the possibility of association due to dipole–dipole interaction is considered then it must be acknowledged that in dilute solutions there are no objective reasons for assuming the existence of hydrogen bridges, provided only that the latter do not exhibit any new properties distinguishable from those for bridges in $(R_2AlH)_x$. For compounds of the type $R_2AlH.N(CH_3)_3$ and $RAlH_2.N(C_2H_5)_3$. another method of association is possible—due to the carbon of the methyl (for R = CH_3) and methylene CH_2 group (for R = C_2H_5). Such a possibility follows from the splitting of the NMR lines[30]. We note that the dimerisation of $Al(C_2H_5)_3$, also investigated by the NMR method[123] also takes place because of the CH_2 group. Doubt about the formation of hydrogen bridges has repeatedly been expressed[16,115,123]. In particular, it is thought[16] that: (a) it is difficult to assume that tetrahedral 1 : 1 complexes lose symmetry and acquire sp^3-spd-hybridisation† with five-coordinated aluminium owing to the formation of hydrogen bridges, and (b) the assumption of dimerisation should imply the presence in the solution of an equilibrium between the monomers and dimers which should enrich the spectra with new lines, which is not observed. True, later the same authors concluded that dimers existed[9], arguing mainly from a comparison of the spectra of $AlH_3.N(CH_3)_3$ and $AlH_3.2N(CH_3)_3$ in the crystalline state, in concentrated and dilute solutions in benzene, and in the gas, and the spectra of $AlH_3.N(C_2H_5)_3$ and $AlH_3.C_4H_8O$ in the crystalline state and in concentrated solution in C_6H_6. In particular they observed the appearance of weak absorption bands in the 1550–1650 cm^{-1} range in concentrated solutions and in the crystals and a displacement of the Al–H frequency to 1762 cm^{-1} for $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ in comparison with the dilute solutions (Table 5). From what has been said above, clearly these results cannot themselves be considered as any significant argument in support of the formation of hydrogen bridges. The discussion of Roszinski and Dautel[9], leading them to conclude the formation of hydrogen bridges, also cannot be considered as substantiated. They found by comparison of the spectra in various states of aggregation that the spectrum of $AlH_3.N(CH_3)_3$ in the crystal differs considerably from its spectrum in the gas, but the spectra of $AlH_3.2N(CH_3)_3$ agree. Hence it was concluded that the first compound in the crystal is dimerised, but the second is not. On comparing further the spectra in the crystal and in the concentrated solution and establishing their similarity, the authors drew conclusions about association in the solution. There are two weak spots in this approach which lead to quite unreliable conclusions. Firstly, it is not explained why associates do not appear in the spectra of moderately concentrated solutions. Secondly and mainly, there is no basis for ascribing the difference in the spectra in the crystal and the gas to associates when there is no additional information about the crystal structure, since the appearance of new frequencies and a displacement of the known frequencies can be due to the deformations of the molecules in the crystal field (this, to a certain extent, also relates to concentrated solutions). Such deformation is observed, for example, for the tetrahedral anions $Al(CH_3)_4^-$ in the field of the cations[108] in the $LiAl(CH_3)_4$ crystals. Moreover, the solid compound $AlH_3.NR_3$ sublimes comparatively readily, which would be improbable in the presence of hydrogen bonds.

Finally, association in benzene solutions of $AlH_2N(CH_3)_2$ and $AlH_2N(C_2H_5)_2$ takes place[31] most quickly due to Al–N–Al bonds by analogy with $BH_2N(CH_3)_2$, where such a structure was found by X-ray diffraction[124].

As regards the structure of the complexes in the crystalline state, here except for $AlH_3.2N(CH_3)_3$, which has been investigated by X-ray diffraction, much is not clear. Table 10 shows the frequencies of the Al–H bonds for several compounds.

$AlH_3.2N(CH_3)_3$ crystals consist of individual molecules of the complex[24] without directed bonds between them[9,16]. The spectra of $LiH.AlH_3$ crystals accord with an ionic structure in which the nodes of the lattice are occupied by tetrahedral AlH_4^- ions with Li^+ ions distributed between them[77]. Possibly there is some distortion of the regular tetrahedral form of the anion in the field of the cation[93], like that observed in $LiAl(CH_3)_4$,[108] and responsible for some complication of the spectrum observed in later investigations[9]. On the basis of a comparison of the infrared spectra of crystalline alkali metal tetrahydroaluminates, the authors[93] consider that such distortion is maximal for $LiAlH_4$ and minimal for $CsAlH_4$, with the symmetry of the former being decreased to C_{2v} owing to the formation by the lithium of covalent bonds with two hydrogens of

† Three tetrahedral sp^3-orbitals; instead of a fourth orbital, two spd-orbitals with an included angle of 71°.

the AlH_4^-. The structure of $CsAlH_4$ is thought to be much more ionic with retention of the tetrahedral structure of the anion. For $AlH_3.OC_4H_8O$ a chain structure is proposed with

$$Al-OC_4H_8O-Al-OC_4H_8O$$

bonds on the following grounds: (1) the compound is insoluble in inert solvents; (2) it does not melt; (3) the frequencies of the vibrations are close to those of the 1 : 2 complexes; and (4) in the spectrum there is no 455 cm^{-1} band, corresponding to the deformation vibrations of the dioxan ring and inactive in the infrared spectrum under

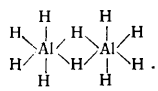
Table 10. Vibration frequencies of the M–H bond of the compounds AlH_3 in the crystalline state, cm^{-1}.

Complex	Vibration frequency	Reference	Complex	Vibration frequency	Reference
$AlH_3 \cdot OC_4H_8O$	1748	9	$AlH_3 \cdot C_4H_8O$	1802	9
$AlH_3 \cdot OC_4H_8O$	1762	16		1810	16
$AlH_3 \cdot LiH$	1778	77	$AlH_3 \cdot 2N(CH_3)_3$	1692	9
	1779	9,13		1702	16
	1782	16	$AlH_3 \cdot LiH \cdot C_4H_8O$	1724	16
$AlH_3 \cdot N(CH_3)_3$	1783	9	$AlH_3 \cdot LiH \cdot 3C_4H_8O$	1695	16
	1786	16	AlH_3*	1592	9
				1600	16

With $(C_2H_5)_2O$ as impurity.

symmetrical loading of the dioxan molecule[16]. For $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ association due to hydrogen bridges is proposed, based on the work[9,16] and their criticism given above. To the critical remarks it must be added that the breadths of the absorption bands in all the instances in Table 10 except AlH_3 are similar. On the other hand the absorption band of AlH_3 is very wide and no narrower than the corresponding bands in $(R_2AlH)_3$.[118,120]

The physicochemical properties of $(AlH_3)_x$ also show its high degree of polymerisation, which is usually connected with a high coordination number of aluminium, namely, 6,[9,13,119,122] leading to the formation of a hydrogen-bridged space lattice, which can be provisionally represented in the form of the fragment:

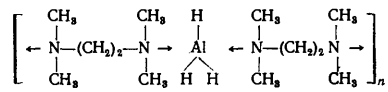


The absorption frequencies of $AlH_3.N(CH_3)_3$ and $AlH_3.C_4H_8O$ —allowing for the fact that they contain a coordinated ligand—lie too high, but for $AlH_3.N(CH_3)_3$ they are still very close to the absorption frequency in the gas (1792 cm^{-1}),[9,26] to support the formation of hydrogen bridges.

Hence it is possible to agree with certain authors[9,16] concerning the polymerisation of AlH_3 due to the formation of hydrogen bridges and to consider their existence at least non-proven in all the remaining complexes of AlH_3. The problem of the structure of the crystals of $AlH_3.LiH.C_4H_8O$ and $AlH_3.LiH.3C_4H_8O$ remains almost completely open.

This section shows rather reliably the existence of compounds of aluminium with coordination number 6, namely, for $(AlH_3)_x$; the same number exists in the complexes which have recently become well-known: Na_3AlH_6 [65,91] and Li_3AlH_6.[82] Six-coordination also may occur in solutions of $AlH_3.MH$ in tetrahydrofuran and diglyme and in a liquid mixture of composition $AlH_3.LiH + 3C_4H_8O$ where the Al–H absorption band is displaced[16] to 1674 cm^{-1}. Most probably, however, it does not exceed 5. In this connection it is interesting to note the remarkable similarity in the structure of the spectra of solutions of $AlH_3.LiH$ in THF and of gaseous $AlH_3.2N(CH_3)_3$ (see Table 11).

However, when the ligand entering the complex is bidentate polymerisation is possible for complexes of AlH_3. Polymeric structures which are well-founded are proposed[10] for complexes of AlH_3 with diamines[10,97]. Thus, a structure with a unit cell containing eight dimeric units:



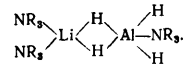
has been given[10] for the complex of AlH_3 with tetramethylethylenediamine.

The high melting points and sublimation temperatures of such complexes and their thermal stability[10,37] also confirm the presence of a polymeric structure. There is probably an analogous structure in the complex of AlH_3 with triethylenediamine[38].

Table 11. Spectrum of a solution of $AlH_3.LiH$ in tetrahydrofuran[16] and of gaseous $AlH_3.2N(CH_3)_3$.[9,26]

$AlH_3.LiH$ in tetrahydrofuran, cm^{-1}	Gaseous $AlH_3.2N(CH_3)_3$, cm^{-1}
1674	1709
895	894
763	793
426	727
416	460

Polymerisation due to ligand has also been proposed for the complex $AlH_3.OC_4H_8O$.[9,16] The complexes $AlH_3.NC_5H_5$,[36] $AlH_3.LiH.N(CH_3)_3$,[88] $AlH_3.NaH.C_4H_8O$,[108] and $AlH_3.LiH.3N(CH_3)_3$[88] are ascribed a structure based on general considerations and chemical properties. It is thought that in these compounds the aluminium has coordination number five and that in the first three complexes the ligand is coordinated by aluminium whereas the last has the structure



Further investigations are needed to establish the complete structure of these compounds.

V. ELECTROCHEMISTRY OF SYSTEMS CONTAINING ALUMINIUM HYDRIDE

1. Electrical Conductivity of Solutions of $MAlH_4$

To show the nature of solutions of hydroaluminates and to make electrochemical preparations information about the electrical conductivity of such systems is needed. The published data are very limited and contradictory.

Solutions of $LiAlH_4$ in diethyl ether have a very low electrical conductivity; κ for a 1 M solution at 15°C is $(4.43 \pm 0.02) \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$,[125] κ for ethereal solutions of $LiAlH_4$ is less by a factor of ~ 2.5 than for such solutions

of $LiClO_4$.[126] The relation between the electrical conductivity of $LiAlH_4$ solutions and their purity has also been noted[127]. The variation of the electrical conductivity with the $LiAlH_4$ concentration is shown in Fig. 1, curve *a*,[127] and agrees in order of magnitude with other results[125]; however, in another study[126] κ is approximately an order

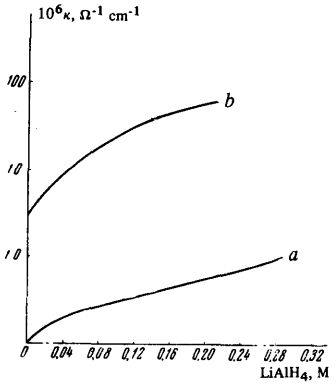


Figure 1. Variation of the electrical conductivity, κ, Ω^{-1} cm^{-1}, with the $LiAlH_4$ concentration: *a*) in pure diethyl ether; *b*) in diethyl ether containing 0.394 M AlH_3.

of magnitude less. Curve *b* shows the variation of κ with $LiAlH_4$ concentration in the presence of AlH_3. Here κ is greatly above the additive value, as with MHal–AlR_3 systems[128]. It is also interesting that the electrical conductivity of ethereal solutions of $LiAlH_4$ and AlH_3 at the same concentrations is similar[127].

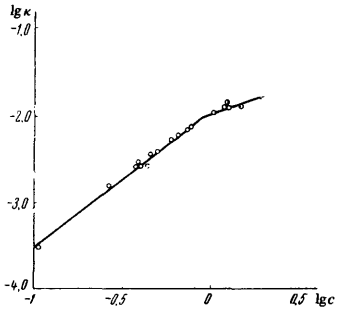


Figure 2. Variation of the electrical conductivity, κ, Ω^{-1} cm^{-1}, of a solution of $LiAlH_4$ in tetrahydrofuran with the concentration *c*, M.

The electrical conductivity of solutions of $LiAlH_4$ in tetrahydrofuran has been measured over the concentration range 0.1–1.5 M at $t = 25° \pm 0.5°C$ (Fig. 2).[129] It was found that such solutions are quite stable even in contact with platinum electrodes.

The variation of the molar conductance with concentration (Fig. 3) does not obey the Ostwald dilution law for weak electrolytes.

Solutions of $NaAlH_4$ in tetrahydrofuran also have high electrical conductivity: $\kappa = 2 \times 10^{-2}\ \Omega^{-1}$ cm^{-1} at $c = 3$ M and 40°C (for 1 mole KCl per dm^3 water $\kappa = 1.10 \times 10^{-1}\ \Omega^{-1}$ cm^{-1} at 25°C [130]).

The electrical conductivity of solutions in tetrahydrofuran greatly exceeds that of solutions in diethyl ether. This is probably because the latter is a weaker complexing agent than tetrahydrofuran in relation to $MAlH_4$, although some effect must be due to the somewhat greater dielectric constant of tetrahydrofuran (7.87) compared with that of diethyl ether (4.34). However, the degree of dissociation of $LiAlH_4$, even in tetrahydrofuran is always small and amounts to 1–10%, which can be estimated from the ebullioscopic value of the molecular weight 38 ± 1 (calculated value 38)[83] and the value of κ on making reasonable assumptions about the mobility of the ions in tetrahydrofuran.

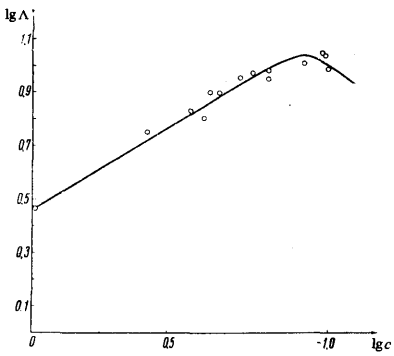


Figure 3. Variation of the molar conductance, Λ_m, Ω^{-1} cm^2 mole^{-1}, of a solution of $LiAlH_4$ in tetrahydrofuran on the concentration, *c*, M.

Most authors assume that $LiAlH_4$ in diethyl ether dissociates into Li^+ and AlH_4^-.[40,125,126,131] However, such a scheme is hardly correct for solutions in tetrahydrofuran. An anomalous dependence of molar conductance[129] of $LiAlH_4$ on concentration‡ can be explained by the complex interaction of the particles of the solute with one another[132,133] or with solvent. The hypothesis of complex formation, probably with participation of the solvent, is confirmed by the fact that the electrical conductivity of dilute solutions of $LiAlH_4$ in tetrahydrofuran has a negative temperature coefficient[129], which could be connected with the breakdown of the compounds formed on raising the temperature. At high concentrations of lithium tetrahydroaluminate in tetrahydrofuran the temperature coefficient of electrical conductivity is greater than zero[129]. Possibly here the increase in electrolytic dissociation of the complexes with rise in temperature exceeds the effect of the breakdown of the complexes into components. On the grounds that the reduction of covalent chlorides (PCl_3, BCl_3, etc.) by lithium tetrahydroaluminate takes place only in the presence of donor solvents, some authors consider that the further dissociation

$$AlH_4^- \rightleftharpoons H^- + AlH_3$$

‡ An increase in molar conductance on increasing the concentration is also observed in solutions of $NaAlR_4$ in diethyl ether (R = alkyl)[84].

is possible[82,125]. The role of the donor here consists in the shift of the equilibrium to the right owing to the bonding of AlH_3 in the complex. It has also been suggested that ethereal solutions of $LiAlH_4$ possibly contain the cations AlH_2^+,[82,134] by the further dissociation

$$2AlH_3 \rightleftharpoons AlH_2^+ + AlH_4^-.$$

The scheme for the breakdown of AlH_4^- with the formation of H^- and AlH_3 seems improbable for energetic reasons although the dissociation of AlH_3 in ether by itself evidently takes place[3]. The latter is confirmed by the conductance of ethereal solutions of AlH_3 (for ~ 0.4 M solution, $\kappa = 3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$).[127] For reasons stated in relation to the compounds $MAlR_4$ (R = alkyl or halogen)[3] it appears that dissociation of $LiAlH_4$ to the H^- ion does not take place. Dissociation with the formation of H^- has also been rejected in another study[135], where the AlH_4^- ion is considered to be the reducing agent. An increase in the reducing ability of $LiAlH_4$ under the influence of donor solvents should evidently be connected with the formation of $LiAlH_4$ complexes which are more active reductants.

The anions AlH_4^- in an ethereal solution of $LiAlH_4$ are probably only slightly solvated in agreement with the instability of the ethereal complexes of $LiAlH_4$ (Table 4) and with the relatively large size of the AlH_4 ion[40] (r = 2.45 Å, calculated on the Al–H distance of 1.66 Å) and also with the absence of a change in breadth and position of the absorption bands of AlH_4^- in the spectra with change of concentration[77,110]. The Li^+ ions in an ethereal solution of $LiAlH_4$ are thought to be strongly solvated[53]. This accords with the weakening of the ether CO absorption bands in the Raman spectra of such solutions[77].

The greater-than-additive values of the electrical conductivity of ethereal solutions of $LiAlH_4$ mixed with AlH_3 (Fig. 1) shows the formation of alternative ions to those arising from $LiAlH_4$ and AlH_3 separately. In accordance with this[3,136] and by analogy with observations on MHal–AlR_3 systems, it is natural to suggest the formation of $MAlH_4.nAlH_3$ complexes or polyhydroaluminates, in particular, heptahydrodialuminate, $LiAl_2H_7$. The dissociation of such complexes should lead to the formation of polyhydrodialuminate ions:

$$LiAl_2H_7 \rightleftarrows Li^+ + Al_2H_7^-$$

and in view of the larger anions the degree of dissociation and consequently the electrical conductivity should exceed the corresponding values for $LiAlH_4$ and AlH_3§.

The relatively high values of the electrical conductivity for the complexes $LiAlH_4.nAl(C_2H_5)_3$ (n = 2–4) and the rise in conductivity with increase in the number of ligand molecules (Ref. 69, see Table 4) also support the hypothesis of the formation of $LiAlH_4.nAlH_3$ in mixtures of $LiAlH_4$ and AlH_3.

2. Electrode Processes

Claisen's patent deals with the electrolysis of solutions of $NaAlH_4$ and $Ca(AlH_4)_2$ in tetrahydrofuran. Mercury was used as cathode and an aluminium rod as anode. During electrolysis sodium amalgam formed on the cathode and AlH_3 accumulated in the solution but at the anode (according to the authors) hydrogen is released by the overall reaction

$$NaAlH_4 \rightarrow Na_{amal} + AlH_3 + \tfrac{1}{2}H_2.$$

It is thought[6] that the accumulation of AlH_3 in solution is accompanied by the formation of the complex $NaAl_2H_7$:

$$2\,NaAlH_4 \rightarrow Na_{amal} + NaAl_2H_7 + {}^1/_2H_2.$$

After the saturation of the electrolyte with the products the "pure" AlH_3 starts to be precipitated. By the term "pure" the author evidently understands AlH_3 free from chloride impurities, as distinct from the hydride obtainable by a chemical method[12]. For the production of unsolvated AlH_3 by this method the hydride cannot be freed completely from impurities, as is evident from the work described earlier. Therefore a similar electrochemical process has no advantages in comparison with the usual chemical preparation.

Information was recently published on the electrolysis of a solution of $NaAlH_4$ in tetrahydrofuran[137]. Several different metals and low-resistance or p-type Ge and Si have been used as anodes, platinum as cathode (Table 12).

Table 12. Behaviour of a series of anions in $NaAlH_4$ + C_4H_8O.

Anode	Current density, mA cm^{-2}	Current efficiency, %	Gas evolution
Mg	9	70	+
Ga	15	100	—
Si	15	124 (Si^{4+})	—
Ge	10—18	13	+
Na	10	not determined	—
Pt, Cu, Hg, Zn	15—22	0	+

Even from a purely qualitative examination of the anodic dissolution of metals it is clear that a sharp difference exists not only between the "noble" and strongly electropositive metals but also between the latter, for example, Mg and Zn. The existence of "free" ions of polyvalent metals in solution is improbable since they tend to form complexes. Moreover, if it is assumed that the initial electrode act is the discharge of AlH^- ions or molecules of $NaAlH_4$ [sic], the atomic hydrogen liberated could form hydrides with the electrode metal. There is therefore a definite probability that in the anodic dissolution of metals hydrides or hydroaluminates of the corresponding metals will be formed. In this connection it is interesting to compare certain properties of these compounds with the ability of the corresponding metals to dissolve during anodic polarisation in solutions of $NaAlH_4$ or $LiAlH_4$ in ethers (Table 13)[134].

By analogy with the solubility of sodium and lithium tetrahydroaluminates it can be suggested that the tetrahydroaluminates of Mg, Ga, and Be are soluble in tetrahydrofuran. Silicon and germanium hydrides are gases and if soluble in ethers the solubility is insignificant. On comparing these results with Table 12 on electrolysis, clearly anodic dissolution occurs for those metals the hydrides or tetrahydroaluminates of which are soluble in the solvent concerned. With germanium the products of

§ After writing this review we learnt that G.Schrauzer (Thesis, Munich, 1956) found an increase in the molar conductance of solutions of alkali metal tetrahydroaluminates with increase in concentration and the electrical conductivity of solutions of $LiAlH_4$ in tetrahydrofuran exceeded the value for a corresponding solution in diethyl ether. He also considers that the dissociation scheme

$$2AlH_3 \rightleftharpoons AlH_2^+ + AlH_4^-$$

is possible.

the anodic dissolution can be removed as gases. With silicon the problem remains unresolved since little gas is released during electrolysis but on the surface a red-brown film forms; this film rapidly turns white and crumbles in air, disclosing a smooth etch surface. Hence, if the proposed hypothesis about the connection of the anodic dissolution of metals with the solubility of their hydrides or hydroaluminates is true, then it could be expected that in this electrolyte not only the metals listed would be soluble, but also Be and Al. The latter was negated by Claisen's results[6], for he did not observe the anodic dissolution of aluminium. However, it should be noted that the patentee did not measure the current efficiency in respect of the metal but the gas liberated, and firstly it is easy to confuse with the boiling of the solvent at the surface of the electrode, and secondly gas liberation is usually observed at the start of electrolysis during the breakdown of the surface film of oxide on the metal.

The process for soluble anodes can then, with some reliability, be described by the equation:

$$M + n AlH_4^- - ne \rightarrow n AlH_3 + MH_n$$

where M is the metal of the anode. It should be noted that the final products of the anodic reaction may be not only the hydride but also $M(AlH_4)_n$. The probability of the formation of the latter depends on its physicochemical properties.

Table 13. Properties of the hydrides and tetrahydroaluminates of certain elements.

Element	$M(AlH_4)_n$	Decomposition temperature, °C	Solubility in $(C_2H_5)_2O$*	MH_n	Decomposition, temperature, °C	Solubility in $(C_2H_5)_2O$*
Mg	$Mg(AlH_4)_2$	~140	+	MgH_2	>200	+
Ga	$Ga(AlH_4)_3$	0	+	GaH_3	>35	+
Al				AlH_3		+
Be	$Be(AlH_4)_2$	>room	+	BeH_2 or $BeH_2 \cdot LiH$	>room	—
Si				SiH_4		
Ge				GeH_4		
Cu				CuH	>60	—
Hg				HgH_2	—125	—
Zn				ZnH_2	90	—
Ag	$AgAlH_4$	—50	—			
Cd				CdH_2	—20	—
In	$In(AlH_4)_3$	>—40	—	InH_3	80	—
Sn	$Sn(AlH_4)_4$	—40		SnH_4		

* + = soluble.
- = insoluble.

At insoluble anodes during the electrolysis considerable evolution of gas is observed, which shows the discharge of hydride ions (molecules). Therefore in this example the anodic process is simpler and can be described by the equation:

$$AlH_4^- - e^- \rightarrow AlH_3 + \tfrac{1}{2}H_2.$$

The electrolytes considered here are extremely complex. Therefore, despite the experimental difficulties further information is necessary, since the mechanism of the reaction can change sharply according to the nature of the anode material. In addition the study of kinetics at insoluble anodes can give interesting information on the hydrogen overpotential for the discharge of hydride ions.

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Progress in the Synthesis of Peptides on Polymers

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CONTENTS

I. Introduction 114
II. Synthesis of polypeptides on polymers 115
1. Essentials of the method 115
2. Synthesis of polypeptides on polymers in the solid phase 115
3. Synthesis of polypeptides on polymers in the liquid phase 118

I. INTRODUCTION

The synthesis of polypeptides is not only one of the present theoretical problems but also a great scientific task and a great economic undertaking. During the last decade in several countries the synthesis of the less complex polypeptides has become attainable not only in laboratories but also on the industrial scale. These are mainly such important biologically active peptides as the hormones oxytocin and vasopressin, which are now easier to synthesise than to isolate from natural sources. The artificial peptide synthesis was developed so that a few years ago three groups of investigators: Katsoyannis and coworkers[1] (USA), Zahn and coworkers[2] (Federal Rupublic of Germany), and Tsou, Wang, and their coworkers[3] (People's Republic of China) succeeded in synthesising the first simplest protein —the hormone insulin, which consists of 51 amino-acids. The complete synthesis of this hormone was effected in 221 stages. This is indeed a great achievement, which itself characterises the modern level of development of peptide synthesis. However, every synthetic chemist knows very well that the multi-stage nature of a synthesis leads to a sharp drop in the yield of the final compound. Thus it is easy to calculate that in carrying out a twenty-stage synthesis with an 80% yield at each stage, the yield of the final product is only 1.2%. In the example of the synthesis of insulin, where the yields were not 100%, the inadequacy of the existing arsenal of methods of peptide synthesis appeared especially sharply.

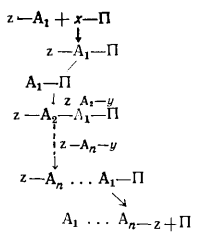
The formation of the peptide bond is only part of the task. A more important obstacle is the purification of the peptide product from impurities formed during the course of the synthesis and which usually have properties very similar to those of the main product. Moreover there is a series of difficulties connected with the low solubility of the peptides in organic solvents, which decreases with increase in the number of amino-acid residues in the molecule. All this placed on the agenda the problem of the creation of more up-to-date methods of synthesising polypeptides. In recent years a way, new in principle, of overcoming the above difficulties has appeared—the construction of peptide chains on three-dimensional polymers in the solid phase and on linear polymers in solution.

II. SYNTHESIS OF POLYPEPTIDES ON POLYMERS

1. Essentials of the Method

In 1959 Merrifield started to develop a new method of synthesising peptides on polymers in the solid phase with the aim of the standardisation and automation of the process. After three years the first report about progress along these lines appeared[4]. Later the synthesis of peptides on polymers was also effected in the liquid phase. The principle of the method is that the first amino-acid $z-A_1$ is attached by a covalent bond to a polymer П. Then amino-acids A_2, A_3, ..., A_n are attached successively to this "anchor" amino-acid. The prepared peptide $z-A_n \ldots A_1-П$ which is formed is separated from the polymer by breaking the peptide–polymer covalent bond at the very end of the synthesis (see Scheme 1, where П is the polymer, z a protective group, A_1, ..., A_n are amino-acids, and x and y are activating groups).

Scheme 1



In the solid-phase synthesis, owing to the insolubility of the peptides attached to the polymer their purification from the starting materials and side-products, even if these impurities are of low solubility, is easily performed by washing with appropriate solvents without danger of loss of peptide. This greatly simplifies the synthesis, shortens the time for carrying out the reaction, and facilitates the purification of the products, so that the standardisation and automation of the processes become possible. The solid phase synthesis allows up to six amino-acid residues to be introduced into a peptide in 24 hours. On using an excess of amino-acid at each stage of the formation of a peptide bond the yield of the peptide usually approaches 100%. Hence the solid-phase synthesis is characterised by simplicity of operation, rapidity, high yields, and the purity of the final products. The synthesis of peptides in the liquid phase on polymers has certain significant differences. Firstly, all the components of the reaction at the time of the synthesis are in the dissolved state but the purification of the polymer–peptide is usually effected by washing free from side-products with water. Secondly, the condensation of amino-acids into peptides is carried out by other methods. In the last stage the peptide separated from the polymer is transferred to an aqueous phase and the polymer remains in an organic layer.

As noted in the very first studies of Merrifield[4,5], the general Scheme 1 is applicable not only to the synthesis of peptides but also to the synthesis of other classes of polymers. Thus, for polynucleotides the individual unit A can be a protected mononucleotide, and for polysaccharides an appropriate protected monosaccharide, etc.

2. Synthesis of Polypeptides on Polymers in the Solid Phase

a. The polymer. In the initial period of the development of the method of peptide synthesis in the solid phase, Merrifield[4,5] carried out considerable work on the selection of a suitable polymer. He tried cellulose, poly-(vinyl alcohol), polymethacrylate, sulphonated polystyrene, and partly chloromethylated copolymer of styrene with 2% divinylbenzene (PSDB–CH_2Cl) which seemed the most suitable for this purpose. Firstly, this polymer is completely insoluble in all the organic solvents used in the synthesis, including neutral, acid, and basic solvents, and at the same time it swells sufficiently in them, which predetermines a rapid penetration of the reagents into the pores of the polymer. Secondly, this polymer has, when swollen, a consistency that is stable and suitable for filtration. Moreover, it contains a functional group capable of reacting with the carboxyl group of the amino-acid or peptide to form an "anchor" covalent bond, which can be split selectively at the end of the peptide synthesis.

b. Protective group and solvent. The success of the synthesis of polypeptides on a polymer basis depends greatly on the choice of a suitable protective group for the amino-acid and of a solvent. In the first studies Merrifield[4,5] protected the amino-components with the benzyloxycarbonyl group (Cbz)†,[6] which is well-known in peptide synthesis and sufficiently readily removable[6]. However, he noted that treatment with hydrogen bromide in glacial acetic acid did not detach all the Cbz groups and that increasing the reaction time led to breaking of some of the "anchor" peptide–polymer ester bonds. For these reasons peptides with shorter chains are formed as impurities and some of the peptide chains are lost. Consequently, it would be necessary either to strengthen the "anchor" benzyl ester bond or to use a more readily removable protective group. Merrifield[4,5] at first followed the first path. For this purpose PSDB–CH_2Cl polymer was nitrated or brominated. As a result of this the loss of peptide due to rupture of the "anchor" benzyl ester bond at the time of removal of the Cbz group became minimal, but the rate of removal of the Cbz groups decreased considerably, especially for the nitrated polymer. On the other hand the polymer–amino-acid bond was strengthened so much that hydrogen bromide in acetic acid had no action on it. Therefore the final peptide was removed from the nitrated polymer by alkaline hydrolysis, and this could lead to a particularly undesirable feature—some racemisation of the peptide. In its properties in peptide syntheses bromination of the polymer occupied an intermediate position.

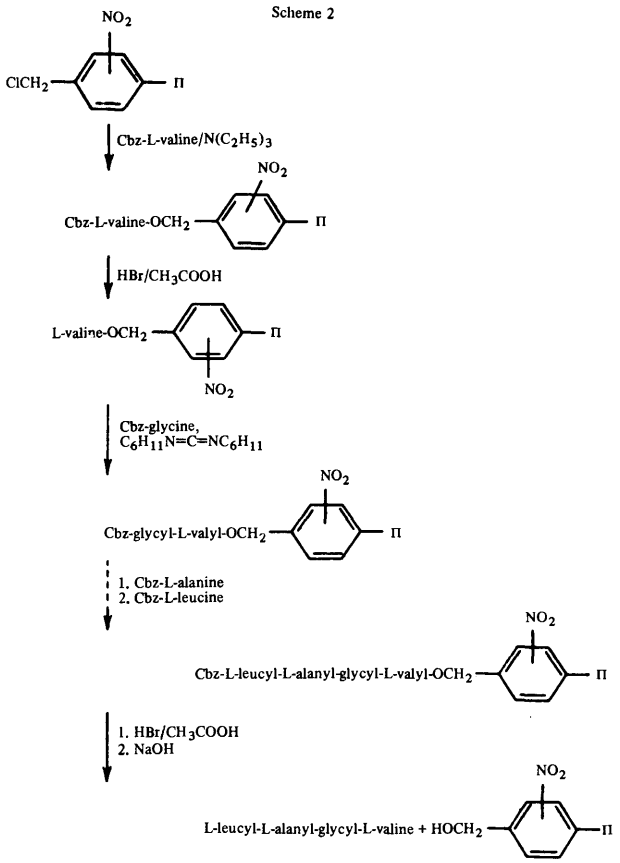
The best solvents in the solid-phase synthesis are dimethylformamide (DMF) and methylene chloride[5], as was shown in studying the synthesis of the tetrapeptide L-leucyl-L-alanyl-glycyl-L-valine on nitrated partially chloromethylated PSDB polymer (Scheme 2, p. 116).

The "anchor" amino-acid Cbz-L-valine was attached by a covalent bond to nitrated PSDB-CH_2Cl polymer by the action of its triethylammonium salt in a suitable solvent; then the protective Cbz group was removed with 10% HBr in acetic acid[7]. After removing all the impurities by washing, DMF was introduced as the best solvent in this synthesis together with Cbz-glycine and the condensing agent, *NN'*-dicyclohexylcarbodi-imide (DCCD). At room

† Cbz is the accepted biochemical abbreviation for the benzyloxycarbonyl (or carbobenzoxy) group (Ed.of Translation).

temperature the reaction lasted 0.5 h. All the side-products, including *NN'*-dicyclohexylurea, were removed by washing with solvents and the Cbz groups were removed as described above. In this cycle the peptide chain is lengthened by one amino-acid. By repeating analogous cycles with Cbz-L-alanine and Cbz-L-leucine the tetrapeptide mentioned above was obtained and was removed from the polymer by hydrolysis with alkali[5], during which partial racemisation of the peptide occurred.

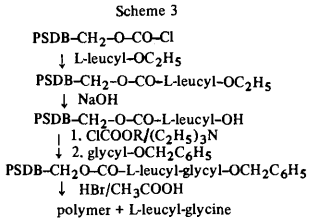
Scheme 2



c. Development of the method. Letsinger and coworkers[8,9] proposed another scheme for the synthesis of peptides in the solid phase. They synthesised a copolymer of styrene with 0.5% divinylbenzene with functional groups which were capable of attachment to the first amino-acid at not the carboxyl, but the amino-group (Scheme 3). This offered the possibility of growing a peptide chain at the unsubstituted carboxyl group of the "anchor" amino-acids by the usual methods. The dipeptide L-leucyl-glycine was obtained in this way.

As we have seen, the strengthening of the "anchor" benzyl ester bond of the polymer–amino-acid did not lead to the desired results. Therefore Merrifield[10] subsequently rejected this path and started to use, instead of a Cbz group, a more readily removable protective group—t-butoxycarbonyl (t-Boc) was introduced into peptide chemistry by McKay and Albertson[11]. In this the solid-phase method not only received a thorough check but was also developed considerably[10,12]. For example, in the synthesis of bradykinin, obtained earlier, particularly by Boissonnas and coworkers[13], polyfunctional amino-acids were included which had been used earlier in solid-phase synthesis: arginine, serine, and proline[10,12]. The solid phase was partly chloromethylated, not nitrated and not brominated, PSDB polymer (Scheme 4). Thanks to the ease of removal of the t-Boc protective groups (1 *N* HCl in acetic acid) the loss of the intermediate peptides was minimised. The use of an excess of t-Boc-amino-acid in the stage of the formation of the peptide allowed the yield of the peptide to be increased and the acetylation with acetic anhydride after each reaction for the formation of the peptide bond previously employed[4,5] to be omitted.

Scheme 3



The final nonapeptide, bradykinin was removed from the solid phase by Gutman and Boissonnas[14] by the action of HBr in trifluoroacetic acid. Note particularly that the synthesis of bradykinin was effected in a special glass apparatus fitted with a system of automatically acting sensors for the initial substances and solvent[15–17]. As a result of the automation of the synthesis the total time required for each cycle was reduced to four hours and the yield of peptide was increased. Thus pure bradykinin with complete biological activity was obtained in 32% yield after 8 days,[10] and in later work[12] in which methylene chloride was used instead of DMF as the solvent, the yield of bradykinin reached 68%.

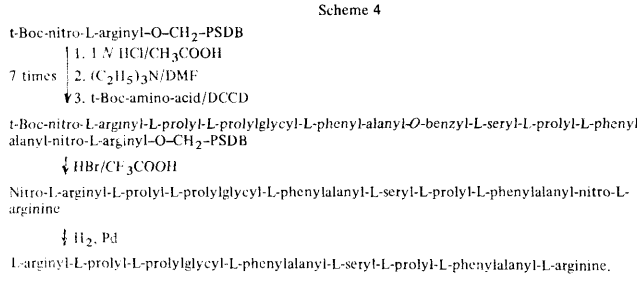
Subsequently Lenart and coworkers[18,19] proposed to remove the prepared bradykinin from the polymer with dry liquid HF in an excess of anisole. In addition to breaking the peptide–polymer ester bond this also removed the NO_2 groups from arginine.

In seeking antagonists for bradykinin, Stewart and Woolley[20,21] used the automatic synthesis of peptides in the solid phase and within an extremely short time obtained 23 analogues of it, including a bradykinin consisting of D-amino-acids. In a completely analogous manner Merrifield[22] added L-lysine and L-methionine to PSDB–CH_2–O–bradykinin and obtained in 65% yield the chemically pure undecapeptide L-methionyl-L-lysyl-bradykinin, with the complete biological activity of natural kinin. During the synthesis the ϵ-amino-group of lysine was protected with a Cbz, not a t-Boc, group. Alkylation of the sulphide group of methionine with the benzyl bromide formed in the action of HBr in CF_3CO_2H on the Cbz group and *O*-benzylserine was avoided by the presence of ethyl methyl sulphide.

The possibility of including any amino-acid in the peptides was of enormous importance for confirming the general applicability of the new method. With this aim general Scheme 4 was used to synthesise in 56% yield the octapeptide 5-isoleucyl-angiotensin II, which exhibits complete biological activity of the natural material, and twice that of

its analogue[23], and also a hexapeptide[24] in which were successfully included four amino-acids not used earlier in the solid-phase synthesis: asparagine, histidine, isoleucine, and tyrosine. It was shown clearly[24] that if the formation of nitriles is avoided[25] asparagine can be added not by the carbodi-imide method but by Bodanszky's nitrophenyl ester method[26], although this method was rejected by Merrifield after some failures[4,5]. This was confirmed by Bodanszky and Sheehan[27], who found that the nitrophenyl ester method can be used on a par with the carbodi-imide method of amino-acid condensation in solid-phase peptide synthesis. True, they did not give any experimental results in support of this. Merrifield's review[28] of the automatic synthesis of peptides considers not only the carbodi-imide but also Nefkens' hydroxyphthalimide method[29] to be applicable and, exceptionally, in some instances Bodanszky's nitrophenyl ester method[26].

Scheme 4



Rothe[30] recently published a brief communication stating that he had succeeded in synthesising, on the basis of a Merrifield solid carrier (true, not automatically), a linear oligomer consisting of 14 monomers of ϵ-aminohexanoic acid. Kusch[31,32] gives more detailed information on the synthesis in a solid polymeric phase of a whole series of analogous linear oligomers of hexamethyleneadipic acid amide:

H–[B–A]–OH, where n = 2–5, and 10,

ω-aminoundecanoic acid:

H(Und)–OH, where n = 2–5 and 10,

and ϵ-aminohexanoic acid:

H–(Cap)–OH, where n = 4 and 8,

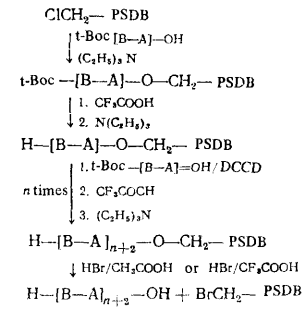
according to Scheme 5, analogous to the general scheme for synthesis on polymers.

The accumulated experience on the synthesis of peptides on solid carriers allowed Marglin and Merrifield[33] to obtain in sufficiently high yields the A and B chains of insulin in 8 and 11 days respectively. However, completely synthetic insulin exhibited insignificant biological activity, since the A chain contained a racemic asparagine residue.

Considerable difficulties are encountered in including in the peptide chain not only asparagine but also serine and also in the removal of *S*-protected groups in peptides. All these problems which arise in the synthesis of long peptides on carriers were discussed in September 1966 in the Netherlands at the Eighth European Symposium on peptides.

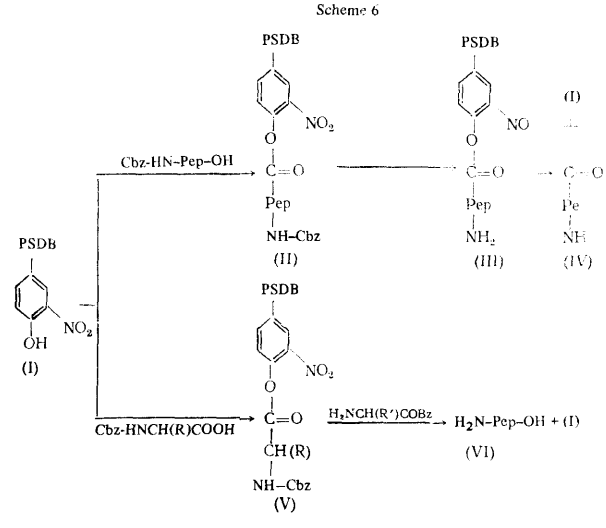
As Katchalski and coworkers showed[34], not only linear but cyclic compounds can be synthesised in the solid phase on polymers. For this purpose poly-(4-hydroxy-3-nitrostyrene) cross-linked with divinylbenzene (I) was obtained, and its active hydroxyl groups were used for preparing high-molecular-weight activated esters of *N*-substituted peptides (II) (Scheme 6).

Scheme 5*



* –A– = –OC.[CH_2]$_4$.CO–;
–B– = –NH.[CH_2]$_6$NH–;
–Cap– = –HN.[CH_2]$_5$.CO–;
–Und– = –HN.[CH_2]$_5$CO–.

Scheme 6



A high yield of activated ester (II) was obtained only on using at least a triple excess of Cbz–HN–Pep–OH‡ and DCCD. After removing the protective Cbz group the formation of the cyclopeptides (IV) occurred, due to intramolecular aminolysis of the ester bond. This method of cyclisation seemed better than the earlier ones since the final cyclopeptides are obtained pure and in higher yields (60–80%).

Polymer (I) (Scheme 6) can be considered as a chemical reagent-activator which is capable of forming with the carboxyl groups of amino-acids or peptides insoluble activated phenyl ethers (II) and (V). Being activated, the

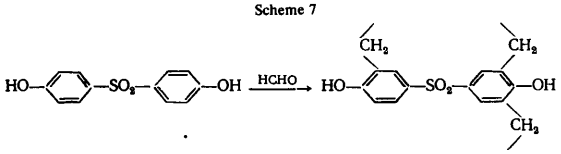
‡ H_2N–Pep–OH is a peptide.

latter can react with compounds which contain unsubstituted amino-groups to form a peptide bond. These considerations were checked experimentally by Katchalski and coworkers [35], and from the insoluble esters (V) Cbz-L-phenylalanine, Cbz-L-proline, etc. were obtained with glycyl–OBz§, S-Cbz-L-cystylglycyl–OBz, etc., the linear peptides (VI) were obtained. At the time of the reaction for the formation of peptides (VI) the initial polymer (I) was liberated and was easily separated from the peptide by centrifuging. By removing the Cbz protective group from the peptide (VI) obtained, it can be introduced again into reaction with the desired insoluble activated polymer with amino-acid (V). On repeating this process a polypeptide of desired structure can be obtained.

Insoluble polymers of phenolic type, one of which contained a mercapto-group in the benzene ring, were made by Shchukina and coworkers [36] and were successfully used for constructing a peptide chain according to Scheme 6.

Wieland and Birr [37] proposed to activate the carboxyl groups of amino-acids with a polymer of phenolic type obtained by the polycondensation of bis-(*p*-hydroxyphenyl) sulphone and formalin according to Scheme 7.

Scheme 7



This insoluble polymer was used to activate Cbz-glycine, t-Boc-L-alanine, etc., which were then used in condensation with the methyl esters of L-phenylalanine and L-valyl-L-phenylalanine.

On detailed examination of all the papers on the synthesis of polypeptides in the solid phase it is easy to note the principal differences in the methods of utilising the polymer phase. In some instances the polymer plays the simultaneous part of a protective group and a peptide carrier from which it is separated at the end of the synthesis, in others the polymer serves as an activating medium and participates in the formation of an amide bond. In the synthesis of peptides by the first path the products were purified by washing the polymer–peptide with solvents and at the end of the synthesis the peptide removed from the polymer was purified in the usual manner. In the second instance the purification of the peptide is possible after any stage, since the peptide which is formed is free from the polymer and present in solution. The synthesis of peptides in the solid phase by the first path, named rightfully after Merrifield, has been greatly standardised and automated. The use of phenol-type polymers for the synthesis of peptides has only started, as we have seen, and will evidently attract even greater attention from investigators in the future.

3. Synthesis of Polypeptides on Polymers in the Liquid Phase

The first studies on the synthesis of peptides on polymers in the solid phase showed certain deficiencies of the method. As we have seen, it can used only when all the reactions are completed rather rapidly and with quantitative yields, since otherwise the final polypeptides separated from the polymer base will be contaminated by peptides of lower molecular weight which are difficult to separate. In turn the rate of formation of peptide bonds and the size of the peptide depends on the permeability of the polymer by amino-acids, peptides, condensing agents, etc. This property is very specific for every concrete instance taken and depends on a series of factors, often not predictable.

With the aim of surmounting the above drawbacks of the solid-phase method, Shemyakin and coworkers [38] proposed the synthesis of polypeptides on linear polymers in the liquid phase. Here the polymer and the growing peptide chain attached to it, just as all the agents, are found in the dissolved state. Partially chloromethylated polystyrene was chosen as the polymeric base (scheme of synthesis analogous to Scheme 2). t-Boc-glycine was attached to it by an ester bond. Then a peptide chain was constructed at room temperature by the method of hydroxysuccinimide esters of t-Boc-amino-acids [39] in DMF. The removal of the excess of the agents and impurities was carried out by washing the precipitated polymer with water and the final tetrapeptide glycyl-glycyl-L-leucyl-glycine, obtained in 65% yield, was detached from the polymer by HBr in CF_3CO_2H.

A second example of the synthesis of peptides, but already cyclic peptides, by the liquid-phase method is the work of Katchalski and coworkers [34]. They synthesised the soluble branched copolymer of L-lysine with 3-nitro-L-tyrosine in which the free amino-groups were blocked by acetylation, and the hydroxyl groups remained free, capable of forming ester bonds with *N*-substituted amino-acids or peptides. However, this polymer had one significant drawback since the high yields of Cbz-*N*-activated esters of type (II) (Scheme 6) could be obtained by using only a considerable excess of Cbz-*N*-peptide. In this connection additional difficulties were created, connected with the removal of the excess of unreacted peptides from a solution. After removing the protective group and the neutralisation of the corresponding hydrobromides an internal aminolysis took place and cyclopeptides were formed in 60–80% yield. In this way cyclo-(glycyl-glycyl), cyclo-(tetra-L-alanyl), etc. were obtained. However, these contained peptide oligomers as impurities, which were not observed in the solid-phase synthesis of cyclopeptides [34].

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In the development of the new method of the synthesis of peptides on polymers in the solid phase the first substantial successes have been obtained. This relates especially to syntheses on PSDB–CH_2Cl polymer, with the use of which the conditions for the combination into peptides of many amino-acids have been studied, including polyfunctional amino-acids, and several linear oligomers of the nylon type have been obtained. It is remarkable that already bradykinin, methionyl-lysyl-bradykinin, angiotensin II, 5-isoleucyl-angiotensin, and several analogues of bradykinin of the L- and D-series have been synthesised. The complete biological activity of the above synthesised products of the L-series confirms the extremely important fact that racemisation does not take place during their synthesis in the solid phase. The high rate and the economic nature of the synthesis results from its considerable standardisation and automation. However, as already noted, the method also has some significant drawbacks and limitations concerning the inclusion in the peptides of asparagine, serine, the removal of *S*-protective groups,

§ Bz = benzyl.

etc. All these problems are now being solved by investigators.

As Merrifield noted[4,5], the solid-phase method allows not only peptides to be constructed on a polymer, but also other oligomers, for example, nucleotides, the first papers about the synthesis of which have already appeared[40-43]. All this suggests that the solid-phase method has enormous prospects. It helps investigators to obtain compounds of the most varied degrees of complexity, having inestimable value not only for theory but also for practice.

Owing to the insufficient information it is at present difficult to state definitely the advantages of the liquid-phase method in comparison with the solid-phase. It must be noted that good results were obtained with this method in the synthesis of oligonucleotides[44,45]. Undoubtedly further investigations in this direction will bring new valuable results.

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The Structure of Conjugated Open-chain Hydrocarbons

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CONTENTS

I. Introduction	119
II. Basic concepts of the structure of organic compounds	120
III. Quantum-mechanical studies of conjugated compounds	124
IV. The vibrational spectra of conjugated compounds	129

I. INTRODUCTION

One of the most important problems in theoretical organic chemistry is the study of the electron density distribution in molecules. Systems with conjugated carbon–carbon bonds occupy a unique position in this problem. Modern theoretical methods of organic chemistry have been their greatest successes when applied to such molecules as polyenes, poly-ynes, aromatic systems (benzenoid and non-benzenoid), organic dyes, and cumulenes. The

phenomenon of conjugation, discovered initially by organic chemists, obtained a theoretical basis with the development of electronic theories in organic chemistry (the Robinson–Ingold concepts[1,2]) and with the application of the quantitative methods of molecular quantum mechanics (quantum chemistry). The study of conjugated compounds by the methods of quantum chemistry always shows displacement of the π-electron density from the multiple bonds to the single bonds even in the ground electronic state of molecules, and the formation of multi-centre orbitals.

Since the nineteen-thirties it has been considered that the experimentally observed physical and chemical properties of conjugated compounds confirm the conclusions regarding π-electron delocalisation, reached on the basis of quantum-mechanical considerations. The concept of delocalisation has been severely criticised, however, particularly in recent years. This criticism is to be found in its most fully developed form in papers by Dewar and Schmeising[3-5] and others[6-12]. It has been shown that many of the experimental facts previously adduced as proof of the delocalisation of π-electrons can be no less successfully explained in terms of the concept of hybridisation, which assumes that the two-centre orbitals of the valency π-electrons are preserved in linear conjugated molecules in accordance with the classical structural formulae. The characteristic features of these compounds are attributed to the differences in the properties of the carbon atoms compared with those in saturated hydrocarbons and compounds with isolated multiple bonds. Attempts have also been made to explain the properties of organic compounds in terms of polar effects and the interaction of atoms which are not joined by valency forces.

It is at present expedient, and quite justified, to regard hybridisation, delocalisation, hyperconjugation, etc. as particular "electronic effects", but it should nevertheless be borne in mind that this separation is to some extent arbitrary and is due to the impossibility of obtaining a rigorous solution of the quantum-mechanical problem for a polyatomic molecule. The above structural concepts attribute a dominating influence on the properties of molecules to one of a number of possible electronic effects. As a result, each of the existing concepts is in principle restricted and in the best circumstances can be used to examine only a definite set of properties for a comparatively narrow range of compounds.

The present review examines theoretical and experimental studies of the structure of conjugated hydrocarbons. On the basis of an analysis of published data, the authors have tried firstly to provide a picture of the electron density distribution in linear polyenes, organic dyes, polyynes, and cumulenes, and secondly to define the limits of applicability of existing concepts of the structure of organic compounds, that is, to show the influence of π-electron delocalisation, the valency state of the carbon, and the interaction of atoms which are not joined by valency forces, on the interatomic distances, bond energies, force fields, and electrical fields of conjugated molecules.

II. BASIC CONCEPTS OF THE STRUCTURE OF ORGANIC COMPOUNDS

In the concept of delocalisation, to confirm the conclusion that the π-electron density is displaced, use is made primarily of the fact that the lengths of the single bonds in polyenes and poly-ynes are much less than the lengths of the C–C bonds in the molecules of saturated hydrocarbons. A basis for comparison was provided by the benzene molecule, in which, with complete delocalisation of the π-electrons, all the carbon–carbon bonds have a length of 1.397 Å, which is intermediate between the length of the C–C bond in ethane (1.54 Å) and the length of the bond in ethylene (1.334 Å). Pauling[13], Mulliken[14], and later Coulson[15] estimated the contribution made by π-electron delocalisation to the decrease in the length of the single bonds, on the assumption that the covalent radii of the carbon in the CC and CH bonds are additive. It was found that the decrease in the lengths of the single bonds in conjugated molecules is due both to the change in the hybridisation of the carbon atoms and to the π-electron delocalisation, to almost equal extents. Dewar and Schmeising[3-5], however, suggest that the additivity rule is not observed in this instance. The decrease in the radius of the tetrahedral carbon atom (C_{sp^3}) on changing to trigonal (C_{sp_2}) and digonal (C_{sp}) is greater in C–C bonds than in C–H bonds. Dewar and Schmeising therefore attributed the decrease in the lengths of the single bonds in conjugated molecules entirely to the hybridisation of the atoms, and not to π-electron delocalisation. On this basis, delocalisation was rejected even in such molecules as butadiene and diacetylene. According to Dewar and Schmeising[4], proof of the absence of delocalisation is provided by the fact that the lengths of the C–C bonds are constant within a given hybrid type (C_{sp^3}–C_{sp^3}, C_{sp^3}–C_{sp^2}, C_{sp^3}–C_{sp}, etc.), irrespective of the nature of the nearest substituents. The observed changes in the lengths of the C–C bonds on going from one hybrid type of single bond to another are strictly proportional to the fraction of "s-character" in the orbitals of the atoms forming the bond (Fig. 1).

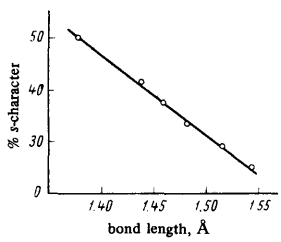


Figure 1. Dependence of bond length on the mean percentage of s-character for single C–C bonds.[4]

A remarkable feature is that the points corresponding to the central bonds of butadiene and diacetylene lie satisfactorily on the straight line. Dewar and Schmeising consider that a linear relationship would not have been expected if delocalisation had a significant influence on the lengths of single carbon bonds. Essentially analogous conclusions were reached as early as 1950 by Tatevskii[16,17], who classified carbon–carbon bonds and established that the bond lengths are constant for each type. A classification of carbon–carbon bonds according to type was also carried out by Herzberg and Stoicheff[18] using spectroscopic data. Later, linear relationships between the length of a bond of any multiplicity and the number of adjacent bonds were observed by Costain and Stoicheff[19] and Bernstein[20]. Moreover, the concept of π-electron delocalisation does not agree with a number of other familiar experimental facts, in particular the similar values found for the lengths

of central bonds with identical hybridisation in the non-planar molecules (in the vapour) of biphenyl and 4,4′-bipyridyl and the planar butadiene molecule[21,22]. Data on bond lengths in the cyclo-octatetraene molecule also do not agree with this concept. Work by Bastiansen and coworkers[23] has shown that in this molecule the single bonds are even slightly shorter than that in butadiene. Moreover, in cyclo-octatetraene (symmetry D_{2d}) the planes of the neighbouring double bonds lie at an angle of ~ 80°, so that the delocalisation of the π-electrons should be very slight, despite the fact that the molecule is an alternant hydrocarbon[24].

Mulliken[25] in his reply to Dewar and Schmeising, agrees that the additive approach to covalent radii is limited, but points out that the classification of carbon atoms in organic compounds as tetrahedral, trigonal, and digonal is also to a considerable extent arbitrary. As shown by Coulson's relationship[26], a condition for the preservation of hybridisation is that the valency angles of the carbon atom remain constant: 109°28′ for sp^3 hybridisation, 120° for sp^2, and 180° for sp. Since the valency angles often differ considerably from these values, a strict subdivision of the hybridisations of carbon into these three types is strictly speaking impossible. This feature was also pointed out by Lide[27].

According to Mulliken[25], the fact that the lengths of bonds with the same hybridisation are constant in conjugated and hyperconjugated molecules does not provide evidence against π-electron delocalisation. The observed facts contradict only the results of the quantum-chemical calculations carried out in the Hückel approximation, and they show complete agreement with the results of modern calculations carried out by various SCF MO LCAO methods[28-32]. The fact that the lengths of C–C bonds of the same hybridisation type are constant, in Mulliken's opinion, is due not to the absence of displacement of the π-electron density from the multiple bonds to the single bonds, but to the fact that the change in the degree of delocalisation in different molecules is small. Some supporters of the hybridisation concept[9-12] reject the existence of delocalisation on the basis of the fact that conjugated molecules do not show an increase in the lengths of the multiple bonds. Mulliken[25] points out that the increases in the lengths of multiple bonds on conjugation, predicted by SCF MO LCAO calculation, do not exceed the experimental errors of even the most precise measurements. Moreover, the lengths of the multiple bonds in conjugated molecules, despite electron delocalisation, may be even shorter than those in non-conjugated molecules. Calculations of overlap populations[33,34] show that the population in the C=C bonds in non-conjugated butadiene is greater than that in ethylene, and this leads to a decrease in the length of the bond; π-electron delocalisation operates in the opposite direction. Thus the double bonds in butadiene may be slightly shorter than the double bond in ethylene, slightly longer than this bond, or almost unchanged, as is in fact observed. Similar conclusions can evidently be reached for the triple bond. For cyclo-octatetraene, Mulliken[14] suggests that the length of the single bond in this molecule is determined not only by the sp^2-hybridisation of the carbon atoms, but also by first-order hyperconjugation.

These arguments are not sufficiently convincing, however. As before, it is difficult, on the basis of the concept of π-electron delocalisation, to explain at least two facts, namely, the linear dependence of the length of the C–C bond on the proportion of "s-character" and the similar values found for the lengths of C–C bonds with the same hybridisation in conjugated and non-conjugated molecules (butadiene, cyclo-octatetraene, biphenyl, etc.). On the other hand, as already noted, the hybridisation concept contradicts the data obtained in all quantum-mechanical studies of conjugated molecules. Dewar and Schmeising[3,4] doubt the reliability of the results of earlier calculations. In their opinion, the increased π-electron density on a single bond, for example in butadiene, is obtained because no allowance was made for the tendency of the electrons to lie on different sides of the nodal plane. A partial correlation related to this tendency is made in calculations by the Pariser–Parr method[35,36], and by Moffit's method[37,38] of atoms in a molecule, by the introduction of empirical corrections into the interelectronic repulsion integrals. The results of calculations for butadiene[28-31] by the methods of Pariser and Parr and Moffit[32,35-37], however, agree with the results of calculations for this molecule carried out by other methods[32-34], indicating that these effects play a secondary role. Moreover, direct calculation with allowance for vertical correlation, carried out by Dewar himself[39] by the split p-orbital method which he developed, gave bond orders for the bonds in butadiene which were very close to the values obtained by the SCF MO LCAO methods[28-31]. Calculations for butadiene by an improved valency bond method, carried out recently by Coulson and coworkers[40], also gave a similar result. Thus the various methods of quantum chemistry are unanimous regarding the problem of π-electron delocalisation in systems of the butadiene and diacetylene type. This however does not yet solve the problem of the lengths of carbon–carbon bonds in organic molecules.

In addition to these two views regarding the reasons for the changes in bond lengths, other ideas have been put forward. For example, Bartell[41-43], opposing both Mulliken and Dewar, considers that the concepts of π-electron delocalisation and hybridisation have no independent significance. In Bartell's opinion, the changes in bond lengths can be attributed to the interaction of atoms which are not joined by valency forces. Bartell considers that evidence in support of his view is provided by the existence of a linear relationship between the length of a C–C bond and the number of nearest substituents in accordance with the change in non-bonded repulsion[43]. The large amount of theoretical and experimental material which has now accumulated, however, shows that interaction between atoms which are not joined by valency forces is not the chief factor determining the lengths of carbon–carbon bonds. Here, reference must first be made to Kitaigorodskii's studies[44-48] of the conformation of organic molecules, carried out over many years. In the mechanical model used for conformational calculations, it is assumed that the optimal conformation is established as a result of a compromise between the tendencies of the molecule on the one hand to keep the values of the valency angles close to the ideal values (109°28′, 120°, and 180° for the sp^3, sp^2, and sp valency states of carbon respectively) and on the other hand to bring the atoms which are not joined by valency forces into equilibrium states. The lengths of the bonds are considered to be absolutely fixed. This approach leads to very good agreement between the calculated and real conformations for a large number of complex, chiefly aromatic, molecules in which the non-bonded repulsion is particularly large. The latest data on the calculation of the optimal conformations of organic molecules by Kitaigorodskii's method are given in papers by Dashevskii[49-51]. Studies[44-51] have shown that the inclusion, in the potential energy expression, of additional terms making allowance for the changes in bond length resulting from the interaction of atoms which are not joined by valency forces is

inappropriate, since the resulting corrections to the bond lengths are insignificant. The results of Coulson's calculations [52,53] of the conformations of "overcrowded" aromatic molecules agree with the conclusion that the bond lengths show little sensitivity to the interaction of atoms which are not joined by valency forces. The same conclusion was reached by Westheimer [54] from an analysis of structural data, and by Wilson [55] from an analysis of the barriers to internal rotation in ethane derivatives.

In addition to data on bond lengths, to which we shall return, results of thermochemical measurements are usually adduced to prove π-electron delocalisation in organic molecules with alternating multiple and single bonds. As early as the nineteen-thirties, Pauling [56] suggested that the heat of formation of a compound can be used as a measure of the strength of the bonding in the molecule. The bond energy was taken as a criterion of bond strength; summation of the bond energies over all the bonds gives the heat of atomisation of the molecule [57]. In organic chemistry the concept of bond energy has been used to determine the additional stabilisation energy of conjugated molecules. The stabilisation or resonance energy was taken as the difference between the heat of atomisation of the real molecule and the additive sum of the bond energies in the corresponding non-conjugated model [14,58]. Another method for estimating the additional energy of conjugated molecules, proposed by Kistiakowsky [59], is based on data on heats of hydrogenation. The resonance energy is obtained by comparing the heats of hydrogenation of the conjugated molecule and a selected model compound, for example, butadiene and but-1-ene, or benzene and cyclohexene. Neither approach can now be considered satisfactory. For the first, the energies of the C–C and C–H bonds are not found to be constant, even in the alkanes [60], and for the second the resonance energy is not entirely an internal characteristic of the molecule, since its magnitude depends on the choice of model compound. The stabilisation energies calculated in this way include effects related not only to electron delocalisation but also to the effects of hybridisation, bond shortening, spatial interactions, etc. Nevertheless, it has been assumed that a predominant part is played by π-electron delocalisation.

In their discussion of resonance energies, as in their discussion of bond lengths, Dewar and Schmeising [3-5] attribute exclusive significance to hybridisation. From calculations based on empirical relationships between bond lengths and bond energies in diamond, methane, and other simple molecules, they concluded that for butadiene the delocalisation energy is equal to almost zero or in the extreme case does not exceed 2 kcal mole^{-1}, and that the total stabilisation energy for butadiene (8.6 kcal mole^{-1}) is due almost entirely to changes in the hybridisation of the carbon. From the same data it follows that the actual delocalisation energy for benzene amounts to not 36 kcal mole^{-1}, but only a quarter of this quantity. Dewar and Schmeising consider that earlier estimates of the delocalisation energy are too high since no allowance was made for the change in the valency state of the carbon atoms and the compression of the σ-bonds.

Mulliken and Parr [61] previously put forward a formula for calculating the heats of atomisation of organic molecules. For C–C and C–H bonds the formula contained empirical constants which did not take account of the changes in the hybridisation of the atoms. Soon after the publication of the paper by Dewar and Schmeising [3], Mulliken [25], introducing additional constants, extended the formula to molecules with C–C and C–H bonds showing different hybridisation. Mulliken's more general formula, like the formula given by Dewar and Schmeising, contains an additional term $E_h = (E'_{CC} - E_{CC}) - 2(E'_{CH} - E_{CH})$, where E and E' are the energies of the bonds formed by sp^3 and sp^2 carbon atoms. The energy E_h acquires a large relative weighting in the total stabilisation energy of the molecule only when the change in the energy of the carbon–carbon bonds with change in hybridisation is much more marked than that for the energy of the C–H bonds. The same assumption was made by Dewar and Schmeising when they suggested that the energies and lengths of the bonds are determined by hybridisation. In Mulliken's opinion, the validity of this assumption is not evident. Mulliken [25] agrees with Dewar and Schmeising that the difference between the heat of atomisation of conjugated molecules and the additive sum of constant bond energies, which is often taken as the resonance energy, is not a true characteristic of delocalisation. He also points out, however, that the approach adopted by Dewar and Schmeising is not rigorous enough to yield unambiguous conclusions regarding the absence of π-electron delocalisation. The same opinion was expressed by Skinner and Pither [62] in a review of thermochemical data for hydrocarbons. Mulliken considers that the theoretical approach to the determination of delocalisation energy appears promising. The calculated energy values can be verified by comparison with the experimental values obtained for the energy barriers to rotation. As an example, Mulliken [61] quotes butadiene, for which the calculated vertical resonance energy amounts to 6.5 kcal mole^{-1}. If this value is corrected for the hyperconjugation for a molecular shape in which the planes of the double bonds are perpendicular, and also for the decompression of the σ-bonds on rotation and the energy of rotation about the single bond in the absence of delocalisation, the calculated potential barrier to rotation amounts to $\sim$ 5 kcal mole^{-1}, which is close to the experimental value [63]. The values of the potential barriers show good agreement with the stability of the planar forms of conjugated systems, produced by π-electron delocalisation. Mulliken's remarks are general in character, however. The theoretical approach to the estimation of resonance energies, expressed, for example, in the LCAO-MO method in units of the resonance integral β, can give only the relative magnitude for different molecules in a series of compounds. As before, the absolute values of the resonance energies remain indeterminate [24]. Experiment shows that even in aromatic systems, steric interactions compete successfully with π-electron delocalisation [44-54]. The frequently encountered departure from coplanarity in aromatic molecules suggests that in linear conjugated systems also, the gain in energy resulting from electron delocalisation constitutes an insignificant fraction of the observed barriers to rotation. Under ordinary conditions, butadiene exists in the *s-trans*-form [64]; the concentration of the *s-cis*-conformation can correspond to only a very small percentage. Calculations by the self-consistency LCAO-MO method [31,32], however, show that the *s-cis*-form of butadiene has a greater stability (from the viewpoint of orbital overlap). Later calculations for this molecule by the SCF MO LCAO method [65] and with allowance for d-orbitals [66] indicate that the stabilities of the two conformations are approximately equal. The fact that butadiene exists chiefly in the *s-trans*-form indicates that a significant part is played by the interaction between atoms which are not joined by valency forces.

Recent papers on bond energies have put forward new calculation schemes, based either [67] on the work of Dewar and Schmeising or on correlations between bond energy and various molecular parameters: the overlap integrals of

the bonding orbitals[68], bond lengths, and bond orders[69,70]. Cox[71,72] extended the relationships obtained by Dewar and Schmeising to organic molecules containing hetero-atoms (O, N, S, and Hal). The data given in these papers, despite the differences in absolute values, change in the same sense as the changes in bond lengths and bond energies. In Table 1 we have compared the most self-consistent values for the energies of bonds of different types. It can be seen from Table 1 that the energy of the single bond in butadiene is almost the same as the energies of bonds of the same type in biphenyl, acetophenone, and biacetyl. The $C_{sp^2}-C_{sp^2}$ bonds in these molecules, however, are known to have significantly different π-orders, so that if a significant part were played by π-electron delocalisation, these bonds should have had different energies. Agreement is also observed between the values of the energies of single bonds of the type $C_{sp^2}-C_{sp}$ in the molecules of phenyl cyanide and vinylacetylene, for which the intermediate

Table 1. Hydrocarbon bond energies.

Type of bond	E, kcal mole^{-1}	References	Type of bond	E, kcal mole^{-1}	References
$C_{sp^3}-C_{sp^3}$	85.0	67	$C_{sp^2}=C_{sp^2}$	133	71
$C_{sp^3}-C_{sp^2}$	89.9	67	$C_{sp^2}=C_{sp}$	135.2*	75
$C_{sp^3}-C_{sp}$	102.4*	73	$C_{sp}=C_{sp}$	150	69
$C_{sp^2}-C_{sp^2}$	98.4* (biphenyl)	74	$C_{sp}\equiv C_{sp}$	167.2*	73
	99.4 (acetophenone)	71	$C_{sp^2}-H$	98.3 (mono-substituted)	
	97.1 (biacetyl)	71		97.5 (di-substituted)	
	98.0 (butadiene)	72			
$C_{sp^2}-C_{sp}$	108.6* (phenyl cyanide)	71		96.6 (tri-substituted)	71
	109.3* (vinylacetylene)	69			
$C_{sp}-C_{sp}$	126.6* (diacetylene)	69	$C_{sp^3}-H$	101.2 (mono-substituted)	72
				100.5 (di-substituted)	
$C_{sp^2}\cdots C_{sp^2}$	113.0 (graphite)	69	$C_{sp^2}-H$	101.8 (benzene)	71
$C_{sp^2}\cdots C_{sp^2}$	117.9 (benzene)	71	$C_{sp}-H$	112.3*	

*Bond energies calculated by the authors using the heats of formation of the compounds and the energies of the other bonds given in the Table. All the values of E relate to 25°C; the values $\Delta H^\circ_{\text{formation}}C(\text{gas}) = 170.9$ kcal g-atom^{-1} and $\Delta H^\circ_{\text{formation}}H(\text{gas}) = 52.09$ kcal g-atom^{-1} are assumed[57].

bonds also have different orders. This shows that the delocalisation energy in conjugated molecules makes up only an insignificant part of the so-called stabilisation energy. When the energies of bonds of the same type are used, the calculated heats of formation of linear conjugated systems almost agree with the experimental values. A different conclusion regarding the part played by π-electron delocalisation was reached on the basis of calculations of the conformation of biphenyl[76,77]. Here it was assumed that the angle of rotation of the benzene rings in the molecule ($\sim$ 41° in the vapour[22]) is determined by the competition between conjugation and the interaction between non-bonded atoms. According to Bartell[78], however, the minimum of the potential barrier for biphenyl shows little sensitivity to the potential associated with electron delocalisation. Change in the latter from 0 to 2 kcal mole^{-1} has almost no influence on the conformation of biphenyl, as can be seen from the published diagrams[76,77]. The non-planar structure of the molecule in the gaseous phase is thus evidently due chiefly to the mutual repulsion of the ortho-hydrogens. In the crystalline state, the planar form of biphenyl is favoured, because of the effects of packing ($\sim$ 3 kcal mole^{-1})[79,80]. Thus the height of the potential barrier to rotation cannot give information on π-electron delocalisation, since this effect is due to a considerable extent to the interaction of atoms which are not joined by valency forces[81-84].

Unlike that for linear conjugated compounds, the delocalisation energy for aromatic molecules, calculated with allowance for the type of bond hybridisation, constitutes a significant part of the stabilisation energy. The value obtained for benzene using the data in Table 1 (comparison with classical cyclohexatriene) amounts to $\sim$ 22 kcal mole^{-1}. It is evidently this feature which makes necessary the introduction of additional terms making allowance for distortion of the aromatic rings in the calculations of optimal conformations by the methods of Kitaigorodskii[44-51] and Coulson[52,53].

The relationship between the energies of bonds of various types (values taken from Table 1) and interatomic distance (Fig. 2) is linear (this was noted earlier[67,71]). The points corresponding to the central single bonds in the molecules of butadiene, vinylacetylene, and diacetylene lie satisfactorily on the straight line. Thus these data on the

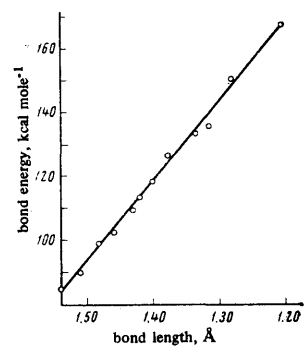


Figure 2. Dependence of the C–C bond energy on bond length.

lengths and energies of the bonds in linear conjugated molecules provide evidence in support of that part of Dewar and Schmeising's treatment which states that these parameters are independent of π-electron delocalisation and can be attributed to the change in the valency state of the carbon atoms. This conclusion does not relate to aromatic compounds. In these compounds, as will be shown below, the π-electron delocalisation is reflected to a marked extent in both the bond lengths and bond energies.

Published explanations of the polarity of conjugated and hyperconjugated molecules are contradictory. Supporters of the delocalisation concept consider that the existence of dipole moments in molecules such as propene and toluene

(~ 0.4 *D*) is due to the displacement of π-electron density. Dewar and Schmeising[3-5] attribute it to the fact that carbon atoms in the sp^3, sp^2, and *sp* states have different electronegativities, according to Walsh[85] and Coulson[86]. On the basis of similar considerations, Petro[87] put forward an additive scheme for calculating the dipole moments of hydrocarbons, in which the C–C and C–H moments were assumed to depend on the type of bond. The possibilities provided by the hybridisation concept in the interpretation of dipole moments are very limited, however. For example, according to this concept the dipole moments of azulene and fulvene should be equal to zero, since all the carbon atoms have the same sp^2-hybridisation, whereas the observed dipole moments are 1.0 *D* and 1.2 *D* respectively[24]. It is just as difficult to explain the polarity of these molecules on the basis of the hybridisation concept as it is to understand, for example, the decrease in the length of the single bonds in cyclo-octatetraene on the basis of the delocalisation concept. The concept of bond delocalisation does not encounter any fundamental difficulties, however, when applied to the dipole moments of non-alternant hydrocarbons (including azulene and fulvene). Hückel's simple MO method and the electron-gas method give very high values for azulene and fulvene (~ 6.5 *D* and 4.5 *D* respectively[88,89]), but the use of improved MO methods with self-consistency gives much better agreement between the calculated and experimental values[24].

Anomalies are observed in the optical properties of hydrocarbons with conjugated multiple bonds. In the electronic spectra this is revealed as a bathochromic shift and increase in the intensity of the absorption bands, and in the Raman spectra it is revealed as a sharp increase in the intensities of the lines due to the vibrations of the multiple bonds. Exaltation of molar refractions is also an optical sign of conjugation in organic compounds. Consideration of these phenomena lies outside the scope of the present review, however, since they are related not only to ground state but also to the excited electronic states of the molecule.

Considerable information on the detailed structure of molecules in the ground electronic state is provided by the radiofrequency spectra. Data on molecular structure recently obtained by NQR, EPR, and NMR methods indicate delocalisation of electrons not only in conjugated and hyperconjugated systems, but even in alkanes. Thus Semin[90], in an NQR study of compounds of the type $Cl-[CH_2]_n-Cl$ ($n = 1-10$) observed a characteristic interaction of the chlorine atoms through the chain of methylene groups. On the basis of calculations in the LCAO-MO approximation, the observed dependence of the NQR signal on the length of the chain was later attributed by Sokolov and Umanskii[91] to partial delocalisation of the σ-electrons of the C–C bond. Proof of delocalisation in hydrocarbons (including alkanes) has also been obtained by EPR[92-96] and NMR[97,98] methods.

In the light of these facts it is evident that none of the existing structural concepts can claim to explain all the varied properties of organic molecules. The non-equivalence of the concepts of hybridisation and π-electron delocalisation in their approach to the study of molecules should be noted, however. In this respect, the concept of delocalisation exhibits the greatest generality. Its conclusions are based on the theory and calculation methods of quantum chemistry. Its range of application is not restricted to individual classes of compound or to definite energy states of molecules. The concept of hybridisation (and the concept of non-bonded interactions), however, is based on a number of empirical relationships and is therefore more particular and simplified.

III. QUANTUM-MECHANICAL STUDIES OF CONJUGATED COMPOUNDS

The success of the application of quantum chemistry to conjugate compounds is due chiefly to the presence of π-electrons, which, in an approximation which is adequate in many instances, can be considered independently. In this section we shall deal with the results of quantum-mechanical studies of linear polyenes, organic dyes, polyynes, and cumulenes.

1. Linear Polyenes

A central problem in the structure of conjugated systems is the question of the change in π-electron delocalisation and the associated change in the lengths of the multiple and single bonds with increase in the length of the chain.

One of the first quantum-mechanical calculations for polyenes was carried out by Lennard-Jones[99,100] using the simple MO method. By using bond length data for ethylene and ethane and determining the resonance integrals for the double and single bonds in polyenes, Lennard-Jones found a decrease in the length of the central bond in butadiene. According to the calculation, the addition of new units to the conjugated chain should lead to gradual equalisation of the bonds. In an infinite polyene the double and single bonds are completely equalised, the length of each being 1.30 Å. Equalisation of the bonds in the central region of a polyene chain also followed from work published simultaneously by Penney[101], who used the valency bond (VB) method. Later, Coulson[102] studied linear polyene radicals $C_{2n+1}H_{2n+3}$ and concluded that as $n \to \infty$, the configurations with alternating bonds will be less stable than those with equalised bonds. In a subsequent paper Coulson[103] extended this conclusion essentially to polyene molecules $C_{2n}H_{2n+2}$, when he found that with increase in *n* for these molecules the orders of the double and single bonds are equalised from the ends of the chain to the centre. In the same paper Coulson for the first time introduced fractional bond orders within the framework of the MO method.

The inadmissibility of the model with equalised bonds for polyenes was soon demonstrated by Mulliken[104,105]. He showed by the simple MO method that for equalisation of the bonds the wavelength of the first absorption band should be proportional to the length of the chain for all conjugated systems, including linear polyenes. The same result was obtained by Kuhn[106] by the simple electron-gas method. It had been known even earlier[107-118], however, that the absorption bands in the spectra of polyenes converge with increase in chain length; with the addition of each unit the bands are displaced towards longer wavelengths by an ever-decreasing amount, tending towards a definite limit (Fig. 3). Kuhn[106,114,115] showed that in order to obtain satisfactory agreement between the experimental and calculated wavelengths in the ultraviolet spectra of polyenes it is necessary to assume strong alternation of the π-electron density in the polyene chain. In the electron-gas method this is achieved by introducing an alternating nuclear potential with maxima in the middle of the double bonds in the classical formula of the polyene. The calculations carried out by Kuhn and coworkers[116] for two- and three-dimensional models showed that the alternation of the electron density in long linear polyenes is the same as that in butadiene.

Dewar[117] studied the electronic structure of polyenes with long chains by the LCAO-MO method. He also showed that in the absence of alternation the calculated frequencies of the absorption bands should tend to zero as $n \to \infty$.

Agreement with experiment can be obtained by assuming that all the double and all the single bonds are equivalent and by assigning different values to the resonance integrals for both types of bond.

Platt[118] attributes the observed regular features in the absorption spectra of linear conjugated systems to the configurational interaction of several possible electronic states. Either the interaction is constant and the compounds have equalised bonds (cyanine dyes) or the interaction varies with chain length, leading to alternation of charge density and hence to alternation of bond lengths. In Platt's opinion, solution by the simple LCAO-MO method

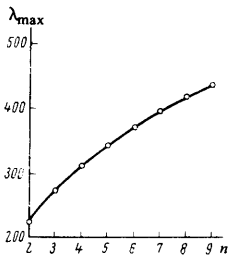


Figure 3. Dependence of λ_{max} (nm) on n for *trans*-polyenes $H_3C-[CH=CH]_n-CH_3$.[113]

leads to equalisation of the bonds in polyenes because no allowance is made for the configurational interaction between the ground and lower excited electronic states. A similar conclusion was reached by Labhart[119] using the free-electron method. He showed that when allowance is made for the compressional energy of σ-bonds the filled π-electron levels of polyenes with alternating bond lengths lie below the levels for polyenes with equal bond lengths. The conclusion that there is alternation of the π-electron charge density on the bonds also follows from the modified potential-box model examined by Bagdasar'yan[120]. Alternation is energetically favourable, since the energy of the electrostatic repulsion of the π-electrons on neighbouring bonds is then minimal.

Ooshika[121,122] was the first to use the semi-empirical Pariser–Parr–Pople SCF MO LCAO method[28,35,36] to solve the problem of the alternation of bond lengths in polyenes. For an infinite polyene chain the π-order of the C=C bond was found to be 0.938, and that of a C–C bond 0.249. These values are very close to the bond orders in butadiene, calculated by Mulliken[25]. Ooshika noted that strong alternation of the bond orders in polyenes leads to an absorption energy difference for an infinite number of double bonds equal to ~ 5.6 eV, although the experimental value is 2.5 eV.[118] Huzinaga and Hasino[123] carried out calculations for polyenes using a modified LCAO-MO method based on a united atom model[124], for which the Coulomb integral depends on the interatomic distance. The authors also obtained significant alternation of the lengths of the double and single bonds (~ 0.1 Å). Thus even in the late nineteen-fifties a large number of quantum-mechanical papers had shown that results agreeing with experiment can be obtained for polyenes only by assuming bond alternation, which is preserved with increase in chain length. Alternation of the bond orders and bond lengths decreases the total energy of the system, making it more stable relative to the system with equalised bonds.

In addition to quantum-mechanical calculations, classical models have been used in the interpretation of the electronic spectra of polyenes. Lewis and Calvin[125] used a model with non-coupled oscillators, but the relationship which they found between the wavelength of the absorption band of the polyene and the number of double bonds did not agree with experimental data[126]. Much better agreement with experiment was obtained by Kuhn[127] and Hirayama[128], who assumed coupled oscillators. In a series of papers by Simpson[129–132] the characteristic features of the structure of polyenes are attributed to the electrostatic interaction of the double bonds. In Simpson's opinion, a significant contribution to the ground state of these compounds is made by an ionic structure with alternating charges, for example, $-\bar{C}=\bar{C}-\bar{C}=\bar{C}$ for butadiene. Simpson's model is, however, extremely far from reality[133].

Among later quantum-mechanical studies of the structure of polyenes, mention must be made of work by Longuet-Higgins and Salem[134,135]. These authors used the simple LCAO-MO method, but they made allowance for the compressional energy of σ-bonds and introduced not the parabolic dependence of the resonance integral β on the interatomic distance, as Lennard-Jones had done[99,100], but an exponential dependence. It was found that with this approach, cyclic and linear polyenes with equalised bonds become dynamically unstable as $n \to \infty$. The theoretical analysis also led Longuet-Higgins and Salem to the conclusion that the molecular π-orbitals in the ground and excited states of an infinite polyene do not form a continuous bond, but are separated by a finite energy barrier. This means that an infinite polyene should behave not as a one-dimensional metal but as an insulator with a low electronic excitation energy. This conclusion is directly related to the chemical problem, examined below, of the mutual influence of atomic groups separated by a chain of conjugated bonds.

Pople and Walmsley[136] calculated the energy of the lower excited state for polyenes by the Pariser–Parr method[35,36] for weak and strong alternation of the bonds. They found that the limit of the long-wave absorption is 2.9 eV for the former, and 4.6 eV for the latter. Thus according to Pople and Walmsley, weak alternation of the bonds shows better agreement with the experimental value of 2.5 eV.[118] Dixon[137] examined the nature of the alternation of bonds in polyenes by the VB method. In contrast to the earlier calculations of Penney[101], the values of the Coulomb and resonance integrals were assumed to be different, depending on the interatomic distance (the method has been described in detail[138]). The lengths of the double and single bonds calculated by Dixon are almost independent of the dimensions of the polyene chain and show good agreement with the experimental bond lengths for butadiene[139,140]. Merz and coworkers[141] used the "molecules in molecules" method, developed by Longuet-Higgins and Murrell[142], to interpret the electronic spectra of conjugated compounds. They concluded that there is considerable localisation of the π-electrons on the bonds in linear polyenes, irrespective of the length of the chain.

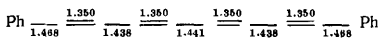
A recent paper by Dewar and Gleicher[143] (see also Refs. 5 and 144) described a study of the structure of polyene compounds by the Pariser–Parr–Pople SCF MO LCAO method and the split p-orbital method[145]. Both methods showed that with increase in the chain-length the alternation of the double and single bonds remains almost the same as that in the first members of the vinyl series. At the same time it was shown that the heats of formation of polyenes can be represented in the form of additive sums of the empirical energies of the C=C, C–C, and C–H bonds. In

the opinion of the authors cited, this indicates the absence of π-electron delocalisation and the inappropriateness of using the actual concept of bond delocalisation or resonance interaction to describe the collective properties of molecules, It is difficult to agree with this, however, since even the energies of aromatic hydrocarbons, in which the existence of resonance interactions cannot be doubted, can be described by additive schemes[146]. As will be shown below, bond energies, like bond lengths, cannot serve as reliable criteria of π-electron delocalisation in linear conjugated molecules.

Calculations of the absorption spectra, ionisation potentials, charges on the atoms, and bond orders in polyenes $H[CH=CH]_nH$ (n = 1–10) and in various condensed aromatic compounds have been described by Adams and Miller[147]. The calculations were carried out using a semi-empirical method in a π-electron approximation which differs from the generally adopted Pariser–Parr–Pople SCF MO LCAO method in that the atomic orbitals are expressed in terms of orthogonal orbitals of the Slater type (after Lowdin). The results obtained indicate that there is strong alternation of the π-electron density in polyenes and that the orders of the double and single bonds depend little on chain length.

Thus quantum-mechanical examination using all existing methods shows that polyenes in the ground electronic state form systems with alternating charge density. The problems of the degree of alternation and the change in bond orders with increase in chain length have been less fully investigated. The quantum-mechanical problem of the transfer of influence along a chain of conjugated bonds has been little studied, although there is an extremely widespread opinion that the polyene chain exhibits metallic conductivity[148].

The problem of the alternation of bonds in long polyenes might be solved unambiguously by experimental methods, but the amount of available material is extremely small. We know of only one X-ray diffraction study, by Dreuth and Wiebeng[149], in which the bond lengths in 1,8-diphenyl-1,3,5,7-octatetraene were determined. It was shown that the molecule has the *s-trans*-configuration with the following bond lengths in the chain:

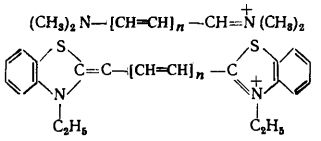


There is very little published information on the structure of excited states of polyenes. This problem was first examined in relation to polyenes by Bayliss[150] and later, in more detail, by Platt[118]. In the excited state of hexatriene according to Bayliss, migration of the charge takes place from the centre of the chain to its ends. The double-bond character of the central bond decreases, and that of the neighbouring single bonds increases. On excitation of the polyene, the alternation of the bonds is preserved, but its sign changes. In Platt's opinion[118], this explains various characteristic features of the absorption spectra of polyenes, in particular the existence of a distinct vibrational structure in the spectra at room temperature.

Recently, Hoffmann[151] carried out calculations on the geometry of polyenes in the first excited state. Using an extended version of Hückel's method which he developed, Hoffmann showed that in the excited state of butadiene the planes of the terminal CH_2 groups are mutually perpendicular. In the excited state of hexatriene, rotation about the central double bond takes place. Octatetraene and polyenes with higher molecular weight remain planar in the excited state.

2. Organic Dyes

From the work examined in the previous section, it follows that the convergence of the wavelengths of the absorption bands observed in the electronic spectra of polyenes with increasing chain length is due to the alternation of bond orders. There is an extensive class of compound, however, whose ultraviolet absorption bands do not show this tendency. These include the symmetrical polymethine (I) and cyanine (II) dyes:



With the addition of a new unit, the absorption band of (I) and (II) is displaced by a constant amount equal to 1000 ± 50 Å [152–162] (Fig. 4). The first attempts to use the methods of quantum chemistry (VB and MO) to interpret the electronic spectra of organic dyes are described in papers by Föster[163] and Herzfeld and Sklar[164–166]. Kuhn[114–116] was the first to show that the observed regular features in the spectra of compounds (I) and (II) can be described satisfactorily by the free-electron method using a model with equalised bonds. The application of the method of molecular orbitals to these compounds is described by Dewar[167].

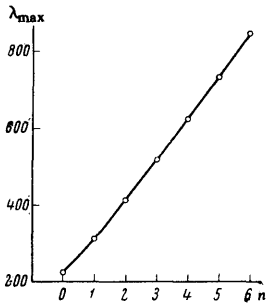


Figure 4. Dependence of λ_{max} (nm) on n for cyanines $(H_3C)_2\overset{+}{N}=CH-[CH=CH]_n-N(CH_3)_2$.[113]

Fukui and coworkers[168] concluded that in order to obtain better agreement with experiment in calculations for symmetrical polymethine dyes by the electron-gas method, it is necessary to assume a slightly modified potential, because of the influence of the terminal groups. A similar conclusion was later reached by Oldzewsky[169,170], who used the potential-box method and introduced barriers associated with the terminal effects of the nitrogen atoms. For a chain of carbon atoms, as in work by Kuhn[114–116], Bayliss[150], and Simpson[171], an equalised potential was used. McGlynn and Simpson[172] calculated the energies of electronic transitions by an improved LCAO-MO method in the Pariser–Parr approximation.

In recent years, new experimental data have been obtained on the electronic spectra of cyanines, oxonols $O=CH-[CH=CH]_n-O$, and merocyanines[173]

$$(CH_3)_2N-[CH=CH]_n-COH.$$

The dependence of λ_{max} on n for oxonols and merocyanines (Fig. 5) shows that these compounds have different structures. Leupold[174] obtained good agreement between the calculated and experimental positions of the long-wave absorption bands for symmetrical polymethines using a modified version of the simple LCAO-MO method (corrections were introduced for the hetero-atoms). The molecular diagrams obtained indicate almost complete equalisation of the bonds, the bond orders being close to the value obtained by the simple MO method for benzene (0.67). Leroy and Nys[175] carried out calculations for various types of cyanine dye by the Pariser–Parr SCF MO LCAO method. By assuming a linear relationship between bond length and bond order, they obtained values for the carbon–carbon bond lengths in cyanine dyes which almost coincided with the CC bond length in benzene (1.397 Å). Thus according to these authors[174,175], dyes of types (I) and (II) are linear analogues of benzene with respect to delocalisation of the bond lengths and bond orders.

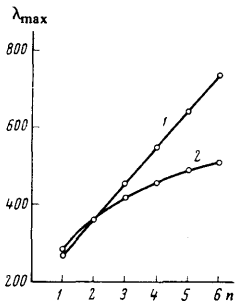


Figure 5. Dependence of λ_{max} (nm) on n for oxonols $O{=}CH{-}[CH{=}CH]_n{-}O^-$ (*1*) and merocyanines $(H_3C)_2N{-}[CH{=}CH]_n{-}CHO$ (*2*). [173]

In a subsequent paper, Leupold and Dähne[176] carried out calculations for oxonols and merocyanines by a method similar to that described earlier[174]. For oxonols, good agreement was obtained between the calculated and experimental bands in the electronic absorption spectra. The CC bond orders for oxonols were also found to be close to the carbon–carbon bond order for benzene. The absorption band maxima calculated for merocyanines[176] showed poor agreement with the experimental values. The experimental data for the electronic spectra of merocyanines[173] and various other unsymmetrical $\alpha\omega$-substituted polyenes[177] show a distinct tendency for the maxima of the long-wave band to approach a finite limit (Fig. 5). This is evidently due to incomplete delocalisation of the π-electrons. Recently, Klessinger[178] carried out calculations for cyanines and merocyanines using the Pariser–Parr–Pople SCF MO LCAO method and showed that these compounds belong to different classes. In the cyanines the bonds are equalised, the π-order approaching 0.67 (benzene) with increase in the chain length. The behaviour of the merocyanines is similar to that of polyenes—considerable alternation of the bonds, which remains almost unchanged with change in the length of the chain, is observed. Alternation of the bond orders in $\alpha\omega$-substituted polyenes is also indicated by dipole moment data[179] and the vibrational spectra (see below). Thus the characteristic features of the electronic structure of linear conjugated molecules in the ground state are clearly revealed in the ultraviolet absorption spectra. Compounds for which the absorption bands in the electronic spectra do not converge with increase in chain length form systems of equalised bonds (cyanines, polymethines, and oxonols). Compounds for which the absorption band maxima tend towards a definite limit with increase in the length of the chain show alternation of electron density (polyenes, merocyanines, and other $\alpha\omega$-substituted polyenes with paired electrons). The limiting wavelength in the electronic spectra is reached more rapidly, the more marked the alternation of the bond orders and hence the smaller the π-electron delocalisation. It is evidently for this reason that the absorption bands in the spectra of *p*-polyphenyls[128], for example, show rapid convergence towards a limit, compared with polyenes. The non-coplanarity of the benzene rings in *p*-polyphenyls, resulting from the interaction of the ortho-hydrogens, leads to greater localisation of the π-electrons within each unit of the chain.

Pouradier[180] analysed a large number of electronic spectra of cyanine dyes, and showed that the distance between the first and second components of the absorption band is approximately constant and amounts to ~ 1200 cm^{-1}, irrespective of the nature of the dye. The splitting was attributed to vibration of the chain in the excited state.

3. Poly-ynes and Cumulenes†

The first calculations for cumulenes were carried out by Pullman and Berthier[181] by the LCAO-MO method with allowance for hyperconjugation of the terminal bonds (after Mulliken[14]).

Quantitative data were obtained on the equalisation of the bonds in cumulenes with odd and even numbers of carbon atoms. It was noted that a bathochromic effect should be observed in the electronic spectra with increase in chain length. Later, again using the simple LCAO-MO method, Longuet-Higgins and Burkitt[182] carried out calculations for the lower polyalkynes (up to and including tetraacetylene) and cumulenes (as far as pentatetraene). The results showed that the poly-ynes and cumulenes show different behaviour with increase in chain length. The equalisation of the orders of the central bonds given by the method of molecular orbitals is slower for poly-ynes than for polyenes. For cumulenes, the bond orders change sharply on going from allene to butatriene, the orders of the terminal bonds decreasing, and the order of the central bond increasing. The bond orders for pentatetraene differ little from those for butatriene; only a slight decrease in the bond orders in the middle of the chain is observed.

The first experimental data on the electronic spectra of poly-ynes and cumulenes were obtained in the nineteen-fifties[183–187]. Comparison of the spectra enabled Krauch[188] to refute the extremely widespread opinion that the electron density distribution is the same for long poly-ynes and cumulenes[189]. If delocalisation of the π-electrons did in fact lead to complete equalisation of the bonds, so that an infinite poly-yne had the cumulene structure, the ultraviolet spectra should have shown a tendency for the absorption bands of molecules of the two classes to approach one another with gradual increase in the number of carbon bonds, but this is not observed. The differences between

† The structures of poly-ynes and cumulenes are considered in the same section of the present review merely for convenience of presentation and not for more significant reasons.

the spectra of these compounds increase with increase in the length of the conjugated chains (Fig. 6). The maxima of the absorption bands for cumulenes, like those of polymethines and cyanine dyes, are displaced regularly by the same amount with the addition of each new unit (for example by ~ 750 Å for tetraphenylcumulenes[187]), whereas the band maxima for poly-ynes, like those for linear polyenes, tend towards a definite limit[183,184].

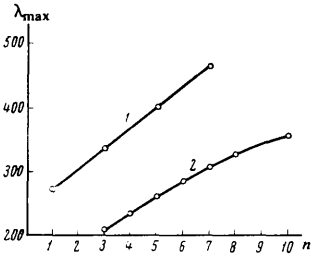
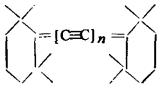


Figure 6. Dependence of λ_{max} (nm) on n for cumulenes



(1)

and poly-ynes $(H_3C)_3C-[C\equiv C]_n-C(CH_3)_3$ (2).[113]

Kuhn[116] examined the characteristic features of the electronic spectra of polyenes and poly-ynes by the free-electron method, using one-dimensional as well as two- and three-dimensional potentials. It was found that all the models give qualitatively similar results for the alternation of the multiple and single bonds in these systems, and that infinitely long polyenes and poly-ynes show approximately the same alternation of bonds as butadiene and diacetylene respectively. It was found that the absorption bands show more rapid convergence towards a limit for poly-ynes than for polyenes. This was reflected in the choice of a larger value for the amplitude of the alternating potential for poly-ynes (3.4 eV) compared with polyenes (2.4 eV). Thus the ultraviolet spectra indicate directly that the electron density distribution is different for poly-ynes and cumulenes. Marked bond alternation, changing little with change in the length of the poly-yne chain, was recently obtained by an SCF MO LCAO method[190] in calculations for the molecules of di-, tri-, and tetra-acetylenes[191,193]. Comparison of the molecular diagrams for these compounds and the molecular diagram for octatetraene[194], obtained by the same method of Julg[190], shows that the electron density distributions in poly-ynes and polyenes are similar.

The structures of cumulenes and poly-ynes have recently been studied by Shustorovich[195-203]. Using the simple LCAO MO method, improved by Longuet-Higgins and Salem[134], Shustorovich obtained data on the barriers to internal rotation in organic cumulenes[195,196], the ionisation potentials and electron affinities[197,198], and the alternation of bond lengths in cumulenes and poly-ynes[199,200]. Shustorovich also examined the electronic structures of cumulenes by the self-consistent π-MO method in the Pople approximation[201]. Despite the large amount of available published material on the electronic spectra of cumulenes, Shustorovich considered only preliminary data on carbene (a compound containing more than 1000 carbon atoms).

Shustorovich concludes that cumulenes and poly-ynes differ only in the structures of the terminal groups, whose influence becomes weaker with increase in the number of carbon bonds. When the chain is sufficiently long, organic cumulenes and poly-ynes are indistinguishable and consist of systems of weakly alternating conjugated bonds. This conclusion, however, does not agree with familiar experimental facts relating to the structures of cumulenes and poly-ynes. It was shown above that available experimental and calculated data on the electronic spectra indicate that there is equalisation of the bonds in long cumulenes on the one hand, and marked alternation of the bonds in poly-ynes on the other. Differences in the structures of these compounds are also indicated by structural data, although such data are at present available only for cumulenes and poly-ynes with a small number of bonds. The bond lengths in molecules of both classes show no tendency to converge (Table 2). If the structures of long cumulenes and poly-ynes were identical, however, the greatest changes in bond lengths with increase in their number should have been observed in these lower members of each series.

Table 2. Bond lengths in cumulenes and poly-ynes, Å.

Compound	References
$C \overset{1.309}{=\!=} C \overset{1.309}{=\!=} C$	204, 205
$C \overset{1.318}{=\!=} C \overset{1.284}{=\!=} C \overset{1.318}{=\!=} C$	206, 207
$C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C$	208
$C \overset{1.205}{\equiv} C$	209
$C \overset{1.205}{\equiv} C \overset{1.378}{—} C \overset{1.205}{\equiv} C$	209
$C \overset{1.20}{\equiv} C \overset{1.38}{—} C \overset{1.20}{\equiv} C \overset{1.38}{—} C \overset{1.20}{\equiv} C$	210

The conclusion that the alternation of bonds in poly-ynes is weak follows inescapably when the version of the simple MO method due to Longuet-Higgins and Salem[134] is used. The simple MO method of Hückel is in general inapplicable to calculations for linear conjugated molecules, since it leads to equalisation of the bonds and to a linear dependence of λ_{max} on the number of multiple bonds[99,100,103], which does not agree with experiment. Longuet-Higgins and Salem, using a slightly improved version of Hückel's method, concluded that there is alternation of the bond orders in polyenes, although for an infinite polyene they also obtained a very small difference between the levels of the ground and excited states (ΔE = 0.25 eV, experimental value $\Delta E \sim$ 2.5 eV [116,118]). Shustorovich[199,200], using the same method, obtained for an infinite poly-yne the value ΔE = 0.05–0.4 eV (depending on the choice of initial parameters), which is also less than the experimental value (~ 3.4 eV [116]).

Hückel's simple MO method, however, describes effectively the electronic spectra of systems with equalised bonds, that is, the spectra of polymethines and cyanine dyes[167], oxonols[176], condensed aromatic systems[211,212], and cumulenes[182,183]. The fact that Hückel's method is applicable to one large group of compounds and is not applicable to another (polyenes, poly-ynes, and merocyanines) is not accidental. It is evidently related to the existence in the first instance, and the non-existence in the

second, of a correspondence between the actual relationship between the energy and the order of the π-bonding and the linear relationship which follows in Hückel's approximation[213]. As shown below, significantly different relationships between the energies and orders of the bonds are observed in these groups of compounds: for cumulenes, polymethines, etc. the relationship is approximately linear, whereas for polyenes and poly-ynes the relationship is more complex.

The characteristic features of the structures of cumulenes and poly-ynes in the ground and excited electronic states were recently studied in detail by Hoffmann[151] using an extended MO method with allowance for σ-electrons. Hoffmann obtained data on the geometry of cumulenes with odd and even numbers of carbon atoms (n) in the ground and excited states. For both states, oscillation of the barriers to rotation (ΔE) depending on n were observed, and it was found that $\Delta E \to 0$ as $n \to \infty$. It was shown that the difference between the energies of the higher filled and lower vacant molecular orbitals (E) is greater for cumulenes with odd values of n than for those with even values; in both instances the value of E approaches zero with increase in n. Hoffmann's calculations agree with experimental data on the excitation energies and electronic spectra of cumulenes. The known experimental values of E decrease regularly in the order: ethylene, allene, butatriene, and pentatriene[214,215]; a linear relationship is also observed between λ_{max} and the number of double bonds[183, 187,216]. Hoffmann studied the electron density distribution using the total charges on the atoms and the overlap populations (n_{ij}). The data which he obtained indicate equalisation of the bonds in cumulenes. For decanonaene ($C_{10}H_4$) Hoffmann obtained the following values of n_{ij} (from the end of the chain to the middle): 1.27, 1.37, 1.32, 1.35, and 1.33. Hoffmann concluded that the poly-ynes show appreciable alternation of bond orders, changing little with increase in chain length. Thus for the poly-yne $C_{16}H_2$ he obtained the following values for the overlap populations n_{ij} (from the end of the chain to the middle): 1.86, 1.01, 1.78, 1.03, 1.76, 1.03, 1.76, 1.03. Hoffmann's calculations showed that in the excited state, unlike acetylene which has the *trans*-form[217-219], diacetylene remains linear, contrary to Pontrelli's conclusion[220].

The structures of butatriene, vinylacetylene, and divinylacetylene were recently studied by Julg and Pellegatti[221] using an improved MO method[190]. For the π-orders for butatriene they obtained the values 0.91 for the terminal bonds and 1.38 for the central bond.

In addition to the literature cited, further references to early work on the electronic spectra of conjugated hydrocarbons can be found in a detailed review by Mason[113]; extensive references on the chemistry of poly-ynes are given in a review by Sladkov and Kudryavtsev[222], and similar references on the chemistry of cumulenes are given in a review by Cadiot, Chodkiewicz, and Rauss-Godineau[223].

IV. THE VIBRATIONAL SPECTRA OF CONJUGATED COMPOUNDS

Isolated attempts have been made to obtain force constants for molecules by quantum-mechanical calculation. The first attempts were made by Coulson and Longuet-Higgins[224] as early as 1948 for the molecules of benzene and butadiene. Calculations within the framework of the simple MO method gave qualitative agreement between the force constants for benzene and the constants determined from the vibrational spectra. Later, Longuet-Higgins and Burkitt[182] used a method developed earlier[224] to calculate the force constants of the carbon–carbon bonds in the molecules of poly-ynes and cumulenes. They noted that the values of the force constants of the bonds are highly sensitive to the π-order, and that the values of the interaction constants are highly sensitive to the mutual polarisability of the bonds. Misurkin and Ovchinnikov[225] recently calculated the vibrational frequencies of the benzene ring using constants found by the MO method. The discrepancies between the calculated and experimental values amounted to several hundred cm^{-1}. This and other work[226-234] indicates that quantum-mechanical methods cannot yet be used to obtain reliable information on the force field of a molecule. As yet, the only real basis for the interpretation of frequencies is the classical semi-empirical theory of vibrations.

The present chapter examines work on the study of the vibrational spectra of conjugated organic compounds. Its aim is to examine the picture of the electronic structure of the molecules revealed by the existing methods of vibrational spectroscopy, that is methods based on experimental data and theoretical concepts which are different from those of the methods of quantum chemistry.

1. Elastic Properties of Conjugated Chains

A large amount of experimental material[139,140,235-237] has been published on the structure of butadiene. Most authors assume that the butadiene molecule can exist in two isomeric forms, the *s*-trans and the *s*-cis. Although the existence of the *s*-trans-form of butadiene is not now doubted, the question of the realisation of the second isomeric form has not yet been completely resolved. The fact that usually only the *s*-trans-form of butadiene exists under normal conditions has been confirmed directly by studies of electron diffraction[139] and the rotational structure of the bands in the vibrational spectra[140].

The normal vibrations of butadiene were first calculated by Sverdlov and Tarasova[238] using the force constants for propene. The marked discrepancy between the observed and calculated frequencies in this and later work by Sverdlov and Tarasova[239] indicates that the force field of butadiene cannot be represented by the additive combination of the force fields of simpler molecules. Recently, Tatevskii and coworkers[240] tried to describe the vibrational spectrum of butadiene by assuming that the elastic properties of the double bonds are the same in the C=C–C=C system and in ethylene. Earlier, Ferigle and Weber[241,242] made an analogous assumption regarding the properties of the triple bond in the C≡C–C≡C system and in acetylene in a calculation of the vibrations of diacetylene and dimethyldiacetylene. To obtain satisfactory agreement with the experimental frequencies of butadiene, Tatevskii and coworkers[240] had to alter significantly the values of a large number of bond–angle interaction constants and increase the constant for the central bond. For diacetylene and dimethyldiacetylene, however, with this assumption, it was necessary to introduce anomalously high values for the constants for the interaction of the triple bonds with adjoining single bonds and also to increase the constant for the central bond. The assumption that the force constants of multiple bonds are the same in conjugated and non-conjugated molecules is unjustified for a number of reasons, including the fact that the constants obtained by Tatevskii and coworkers[240] for butadiene and by Ferigle and Weber[241,242] for diacetylene do not show the continuity required by actual sets of force constants in the description

of the properties of the molecules of a homologous series. The vibrational frequencies for polyenes and poly-ynes calculated using these constants not only show poor agreement with the observed frequencies but also show regular features which are different from those found for the observed frequencies with increase in the length of the chain[243,244]. Sufficiently reliable data on the force fields of compounds with alternating multiple and single carbon–carbon bonds evidently cannot be obtained on the basis of even a correct study of single molecules.

In a study of the structure of conjugated hydrocarbons, the authors of the present review carried out an analysis of the vibrational spectra of a large number of conjugated molecules of various classes: linear polyenes, poly-ynes, vinylacetylenes, cumulenes, and conjugated nitriles. The vibrational spectra of molecules with known structures were calculated for comparison.

The spectra of C_6H_6 and C_4D_6 were used in a study of butadiene[245,246]. In the calculation of the force constants, allowance was made for the characteristic frequency and form for individual atomic groups of many of the vibrations of butadiene. The set of force constants obtained for butadiene was subsequently tested for the molecules of polyenes with higher molecular weight. The constants were also further verified by calculating the electro-optical parameters and integral intensities of the absorption bands in the infrared spectra of C_4H_6, C_4D_6, and other polyenes.

The set of force constants found for the C=C–C=C system[245] indicates that there is appreciable interaction between the carbon–carbon bonds in the ground electronic state of butadiene. The force constants of the C=C bonds were found to be significantly lower than the analogous constants for ethylene[247], propene[248], and 2-methylpropene[249] (12.00 compared with 14.20‡) whereas the constant for the central C–C bond was found to be greater than that for propene and 2-methylpropene (10.40 compared with 7.02); higher values were obtained for the constants for the interaction of the double bonds (–1.50) and the interaction of the double and single bonds (0.40).

The force constants of butadiene were used to describe the vibrational spectrum of 1,3,5-hexatriene[245]. The frequencies of hexatriene calculated on this basis show satisfactory agreement with the experimental values. Complete agreement with the observed vibrational frequencies for the chain of carbon atoms in hexatriene was obtained by correcting slightly the force constant for the interaction of neighbouring double bonds and by making allowance for the weak interaction of the terminal carbon–carbon bonds. Hence the differences in the frequencies of butadiene and hexatriene are due not to a change in the force field resulting from the greater delocalisation of the π-electrons with increase in the length of the chain, as claimed by Lippincott and coworkers[250], but to the purely kinematic factor.

The problem of the equalisation of the bonds in polyenes containing a large number of units was examined by Ivanova and the authors[243] by analysing the vibrations of molecules of the type $X-[CH=CH]_n-X$, where $X = COOC_2H_5$, and $n = 2-8$. Studies of the chemical properties[244] and electronic and vibrational spectra[177,251–253] indicate that these compounds are linear polyenes with transoid arrangement of the bonds. The vibrations of molecules with two to eight units were calculated[243] using three different types of sets of force constants for the polyene chain: those of butadiene[245], propene[248], and benzene[254]. It was found that the calculation reproduces the characteristic features of the experimentally observed infrared[252,253] and Raman[251,252] spectra only when the force constants of butadiene are used. Thus increase in the length of the polyene chain does not lead to significant redistribution of the force field of the molecule.

The force fields of poly-ynes were studied by Popov and Lubuzh[255]. Attempts to describe the vibrational spectra of diacetylene and a number of other poly-ynes containing up to six triple bonds in the chain, using the constants for simple molecules, did not give satisfactory results, as in the case of the polyenes. The force field of the butadiene system C≡C–C≡C was found by simultaneous solution of the secular equations for diacetylene and dimethyldiacetylene. The values obtained differ significantly from the corresponding constants for saturated hydrocarbons and molecules with an isolated triple bond. Thus the force constant of the C≡C bond in diacetylene was found to be less than the constant for acetylene and methylacetylene (22.20 compared with 24.50 [256,257]), and the constant for the central C–C bond was found to be significantly greater than that for the single bond in methylacetylene (11.80 compared with 8.00 [257]). Significant values were obtained for the constants for the interaction of the triple bonds (–1.50) and the interaction of the triple and single bonds (0.50).

The vibrations of the poly-yne chain in the compounds $R-[C\equiv C]_n-R$, where R = Alk and $n = 2-6$, can be described[225] using force constants whose values are extremely close to those for diacetylene and are independent of chain length. This indicates that in the poly-yne chain, as in the polyene chain, equalisation of the orders of the multiple and single bonds does not take place with increase in chain length. This conclusion regarding the structures of linear polyenes and poly-ynes, based on an examination of their vibrational spectra, agrees with the results of most quantum-mechanical calculations and also with the available experimental data on the electronic spectra (the convergence of λ_{max} with increase in n) and bond lengths (the fact that the lengths of the multiple and single bonds are independent of chain length) for these compounds. It should be noted that the differences in the values of the force constants for the C=C bonds in ethylene and polyenes and for the C≡C bonds in acetylene and poly-ynes are not incompatible with the equality of the lengths of the multiple bonds in the corresponding molecules (with the significant interaction constants in conjugated molecules)[258].

Thus analysis of the vibrational spectra of butadiene[245] and diacetylene[255] and of polyenes[243] and poly-ynes[255] with higher molecular weight showed that molecules with alternating multiple and single carbon–carbon bonds have a characteristic type of force field. The force field of vinylacetylene[259] also belongs to this type. Let us consider the factors which may be responsible for the specific features of the force fields of these compounds. Table 3, taken from our paper[266], compares the most important characteristics of the force field for the chains of carbon atoms in butadiene and diacetylene with the analogous characteristics of molecules for which significant electron delocalisation is not expected (compounds *1–7*) and compounds for which delocalisation has been assumed (compounds *8* and *9*). The data show that change in the valency state of the carbon atoms does not lead to a significant change in the force constants for the single and multiple bonds. The force constants for the multiple bonds remain almost unchanged when an H atom is replaced by a methyl group. The constants for the interaction of even adjacent bonds are very small for compounds *1–7*. Quite different relationships between the force constants are observed in the benzene molecule and in the pentadienyl

‡ Here and subsequently the force constants are given in units $\times 10^6$ cm^{-2}.

ring of ferrocene, that is, with complete delocalisation. In this instance there is a change in the constants for the carbon–carbon bonds and a sharp increase in the constants for the interaction of adjacent bonds, and significant values are observed for the constants for the interaction of bonds without a common atom.

Table 3. Force constants of carbon-carbon bonds (in units $\times 10^6$ cm^{-2})*.

No.	Compound	Group	K_i	K_j	K_{ij}	K_{ik}	Type of force field	Refs.
1	ethane	C—C	7.0	—	—	—		260
2	propane	C—C—C	7.0	7.0	<0.1	—		261
3	ethylene	C=C	14.2	—	—	—	non-conjugated	247
4	propene	C=C—C	14.2	7.0	0.1	—		248
5	acetylene	C≡C	24.5	—	—	—		256
6	methylacetylene	C≡C—C	24.5	8.0	0.1	—		257
7	allene	C=C=C	15.0	15.0	0.2	—		262
8	benzene	C⋯C⋯C⋯C	11.4	11.4	1.0	—0.9	aromatic	254
9	pentadienyl ring of ferrocene	C⋯C⋯C⋯C	10.2	10.2	1.0	—0.8		263
10	butadiene	C=C—C=C	12.0	10.4	0.4	—1.5	mesomeric	245
11	diacetylene	C≡C—C≡C	22.2	11.8	0.5	—1.5		255
12	acrylonitrile	C=C—C≡N	13.8	9.5	0,5	—0.1	inductive	264
13	cyanoacetylene	C≡C—C≡N	24.3	10.2	0.7	—0.3		265

* K_{ij} is the adjacent bond interaction constant, and K_{ik} the interaction constants for bonds without a common atom.

Comparison of the elastic characteristics of simple molecules leads to the conclusion that the force constants of carbon–carbon bonds are parameters which are extremely sensitive to π-electron delocalisation but which have a comparatively low sensitivity to change in the hybrid type of the bond. It is therefore natural to relate the specific features of the force field of butadiene and diacetylene not to the hybridisation of the carbon but to partial π-electron delocalisation.

Relationships between the bond order and force constant (Fig. 7) and between the bond hybrid type (or length) and force constant (Fig. 8) have been obtained for single and multiple carbon–carbon bonds[265]. Curve *2* in Fig. 7, based on the relationship between force constant and hybridisation for a single C–C bond, shows the contribution of the σ-components to the values of the constants for multiple bonds (in the harmonic approximation and assuming additivity of the σ- and π-electrons). Comparison of curves *1* and *2* shows that the increased rigidity of the bond with increase in its order is due chiefly to the π-electrons. The values of the π-orders of the bonds, found from the curves in Figs. 7 and 8, amounted to 0.40 and 0.80 for butadiene, 0.45 and 1.88 for diacetylene, and 0.45, 0.80, and 1.88 for vinylacetylene. A noteworthy feature revealed by comparison of these data is the similarity in the values for the orders of the single bonds in butadiene, diacetylene, and vinylacetylene. This indicates that the multiplicities of the central bonds in these molecules are approximately the same. If the decrease in the lengths of single bonds situated between double and triple carbon–carbon bonds were determined to a significant extent by the values of their π-orders (in accordance with the delocalisation concept) we would expect only a very slight difference in the lengths of the C–C bonds in butadiene, diacetylene, and vinylacetylene (not more than 0.03 Å, if we calculate the covalent radius of carbon from data on the lengths of CH bonds). This is not the case, however. On going from butadiene to diacetylene, the length of the single bond decreases by 0.11 Å, which is almost twice that observed on going from ethane to butadiene (~ 0.06 Å).

Conjugated nitriles, such as cyanogen, cyanoacetylene, and cyanoethylenes, which have a formal resemblance to the corresponding conjugated hydrocarbons, are of considerable interest in the further study of this problem.

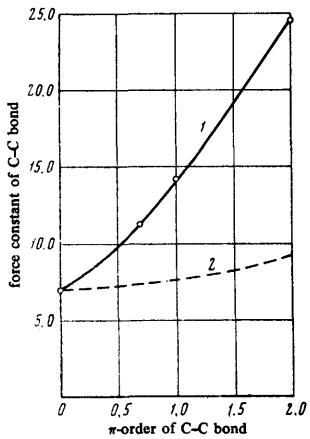


Figure 7. Plot of bond order against force constant for C–C bonds.

Qunatum-mechanical calculations which have been carried out for these molecules do not yet permit an unambiguous conclusion to be reached regarding the electron density distributions. McLean and Clementi[267,268], using the SCF MO LCAO method with allowance for all the electrons, obtained molecular wave functions for hydrogen cyanide (HCN) and cyanogen (C_2N_2). The bond orders for cyanogen calculated on the basis of these results by Mulliken[269] indicate that the delocalisation of the π-electrons in this molecule is as extensive as that in diacetylene. A different

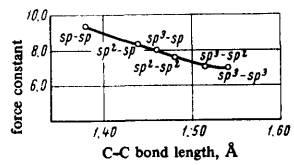


Figure 8. Plot of bond length against force constant for C–C single bonds.

conclusion was reached by Burnelle[270], who also applied the wave functions of McLean and Clementi to the HCN and C_2N_2 molecules. Burnelle concluded that the electron density curves for the HCN and C_2N_2 molecules are almost identical in the region of the nucleus of the nitrogen atom and in the region of the unshared pairs, and also in the zone of the C≡N bonds. Moffat[271] used the LCAO MO method with self-consistency to calculate the orders of the

C=C, C≡C, C–C, and C≡N bonds for an extensive series of nitriles. By assuming that the Coulomb and resonance integrals of the molecules studied are proportional to the corresponding integrals for benzene, Moffat obtained high π-orders for the C–C bonds in acrylonitrile (0.45), cyanoacetylene (0.36), and cyanogen (0.31). Shvarts[272] studied cyanoethylenes by the LCAO MO method and concluded that with increase in the number of nitrile groups attached to the double bond there is a decrease in the π-order of the latter and an increase in the conjugation energy.

The authors of the present review recently carried out an analysis of the vibrational spectra of cyanogen, cyanoacetylene[265], and mono-, *trans*-di-, *cis*-di-, tri-, and tetra-cyanoethylenes[264]. The observed values of the constants show that the force fields of conjugated nitriles differ qualitatively from the force fields of conjugated hydrocarbons. The constants for the bonds in cyanogen, cyanoacetylene, and cyanoethylenes were found to be much closer to the values of the corresponding constants for simple molecules than is the case for butadiene, diacetylene, and vinylacetylene. The values of the constants for the interaction of the multiple bonds are also much smaller. The orders of the central C–C bonds in the above nitriles are smaller by a factor of 3–4 than those for conjugated hydrocarbons. Thus the analysis of the vibrational spectra indicates that the π-electron delocalisation resulting from the intramolecular mutual influence of the nitrile groups and the double (or triple) bonds is not as extensive as that in analogous systems with alternating multiple and single carbon–carbon bonds. In spite of this marked difference in the π-electron delocalisation, the lengths of the single bonds with the same hybridisation in nitriles and in hydrocarbons show almost no differences. Thus here, as in butadiene, diacetylene, and vinylacetylene, we reach the conclusion that the interatomic distances are determined chiefly by the valency state of the carbon atoms, and not by π-electron delocalisation. This is also in accordance with a number of other experimental facts already mentioned. Data on the bond lengths for cyclo-octatetraene, in which the conditions necessary for conjugation are absent, are of particular interest. Our calculation of the force constants for the cyclo-octatetraene molecule[266] confirm that there is very little π-electron delocalisation.

The conclusion that the length of a carbon–carbon bond in linear conjugated systems shows little sensitivity to change in the bond order is not always correct, however. Studies of organic dyes[174,175,178], cumulenes[204,205], and condensed aromatic hydrocarbons[211,212] have shown that the bond orders in these molecules serve as an accurate indication of bond lengths. For example, for ovalene, which has twelve types of non-equivalent carbon–carbon bond, Buzeman[273] obtained excellent agreement between all the experimental and calculated bond lengths. The latter were determined using the π-orders calculated by the simple MO method. It is evident that here, as in many other instances, the agreement is not accidental. Thus at first sight there appear to be contradictory facts, some of which indicate that there is a relationship between bond order and bond length (aromatic compounds, polymethines, cyanines, and cumulenes), whereas others indicate that the bond length is not determined by the bond order (linear polyenes and poly-ynes). The authors of the present review[265] showed that this is due to the specific values of the π-orders of the bonds in the molecule and to the nature of the relationship between the order of a carbon–carbon bond and the change in its length due to π-electrons. The relationship observed[265] is given by curve *II* in Fig. 9. In the construction of curve *II* it was assumed that the lengths of pure σ-bonds of the types C_{sp^2}–C_{sp^2} and C_{sp}–C_{sp} are equal to the lengths of the central bonds in butadiene (1.483 Å) and diacetylene (1.379 Å). The length of a σ-bond of the type C_{sp^3}–C_{sp^3} is equal to the length of the C–C bond in ethane (1.54 Å). The vertical axis on the right gives the differences in the lengths of the multiple and single bonds formed by carbon atoms with the same hybridisation, and the horizontal axis gives the bond orders. As starting compounds we took acetylene, ethylene, benzene, graphite, and ethane, for which the hybridisation, orders,

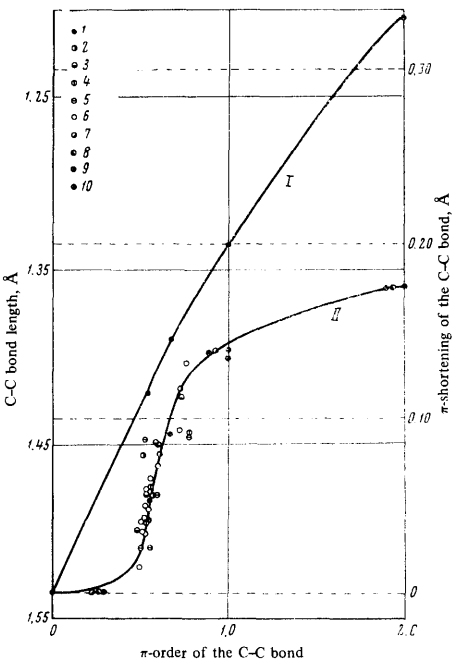


Figure 9. Plot of bond order against bond length (*I*) and bond order against π-shortening of the bond (*II*):
1) Ethane, graphite, benzene, ethylene, acetylene; *2*) naphthalene; *3*) anthracene; *4*) coronene; *5*) pyrene; *6*) ovalene; *7*) butadiene; *8*) diacetylene; *9*) vinylacetylene; *10*) allene.

and lengths of the bonds are known. Thus curve *II* gives the change in the length of the carbon–carbon bond due entirely to the π-electrons. The total change in bond length on going from ethane to acetylene is shown by curve *I* (the familiar Pauling curve). The fact that curve *II* is S-shaped indicates that the lengths of the carbon–carbon bond are not equally sensitive to bond order. The changes in bond order from 0 to 0.4 and in the regions around 1.0 and in around 2.0 lead to small changes in bond length, within the limits of experimental error. It is evidently for this reason that the bond lengths in butadiene, diacetylene, and vinylacetylene (whose bond orders lie in these ranges) differ little from the lengths of the carbon–carbon bonds of the same hybridisation type in molecules in which there is no π-electron delocalisation.

The bond length is most sensitive to change in bond order in the range 0.4–0.9, that is, in the range corresponding to aromatic compounds and organic dyes. Since all the carbon–carbon bonds in these molecules have a

hybridisation close to sp^2–sp^2, the interatomic distances depend almost exclusively on the bond orders, the relationship being almost linear. Curve *II* in Fig. 9 passes through the points corresponding to the molecules of naphthalene, anthracene, coronene, pyrene, and ovalene, and also the points corresponding to the molecules of butadiene, diacetylene (and hence other linear polyenes and poly-ynes), vinylacetylene, and allene.

The observed relationship between bond length and bond order shows that π-electron delocalisation and the associated changes in the orders of the single and multiple bonds in linear polyenes and poly-ynes does not lead to a significant change in bond length. The decrease in the length of the single bonds in these molecules with isolated multiple bonds is determined chiefly by the valency state of the carbon atoms. At the same time, preservation of the lengths of the bonds of a given hybrid type in the molecules of organic compounds cannot be taken as a sufficient basis for rejecting π-electron delocalisation.

This conclusion is equally applicable to bond energies. It can be seen from Fig. 10 that the relationships between bond order and total bond energy (curve *1*) and between bond order and the energy introduced into the carbon–carbon bond by the π-electrons (curve *2*) are analogous to the corresponding relationships between bond length and bond order (Fig. 9). The construction of the curves in Fig. 10 is analogous to that of the curves in Fig. 9; the values of the bond energies are taken from Table 1. The

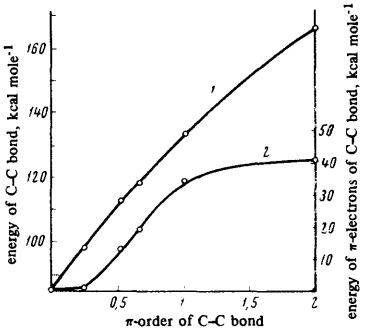


Figure 10. Plot of bond energy against bond order (*1*) and π-bond energy against bond order (*2*).

fact that the bond energy and bond length show identical behaviour with change in bond order is not surprising, since there is a linear relationship between them (Fig. 2). Fig. 10 shows that in conjugated hydrocarbons with open chains the energy of the π-bond is not proportional to the bond order, as follows from the simple Hückel method[213]. This feature evidently explains the overestimation of the part played by π-electron delocalisation in the interpretation of the properties of polyenes and poly-ynes by the Hückel method.

2. Polar Properties of Conjugated Chains

To obtain a more detailed picture of the electron density distribution along a chain of conjugated bonds, it is of considerable interest to study the intensities of infrared absorption bands and Raman lines. According to the modern semi-empirical theory of intensities[274], the electro-optical parameters characterising directly the electronic structure of a molecule are the dipole moments and polarisabilities of the individual bonds and their derivatives with respect to the vibrational coordinates.

The specific form of the electric field of butadiene was determined by the authors of the present review[275] by analysing the intensities of the infrared spectra of the C_6H_6 and C_4D_6 molecules. It was shown that the double bonds in butadiene have dipole moments of ~ 1.3 D, whose positive ends are the $C_{(2)}$ and $C_{(3)}$ central atoms. The parameter which characterises the change in the C=C moment on elongation of the double bonds was also found to have an appreciable magnitude. Since all the carbon atoms in the molecule are in the same valency state (sp^2), the results indicating non-equivalence of the electron density distribution in the C=C–C=C system contradict the views of Dewar and Schmeising[3-5] regarding the structure of butadiene. The observed electro-optical parameters of the terminal $=CH_2$ groups of butadiene (like the $=CH_2$ force constants) differ from the corresponding quantities in non-conjugated molecules (ethylene and propene) to a much smaller extent than the parameters of the central =CH bonds. This suggests that partial delocalisation of the electrons in butadiene and the production of an excess of negative charge on the $C_{(1)}$ and $C_{(4)}$ atoms relative to $C_{(2)}$ and $C_{(3)}$ take place chiefly as a result of the overlap of the π-orbitals of the $C_{(2)}$ and $C_{(3)}$ central atoms. An analogous conclusion regarding the polarity of the multiple bonds and the nature of the electron density distribution was reached by studying the intensities of the infrared absorption bands of other simple conjugated molecules—diacetylene and vinylacetylene[276].

Let us consider briefly the picture of charges on atoms following from quantum-mechanical calculations. Coulson and Rushbrooke[277] previously showed that the π-electron charges on all the carbon atoms in polyenes are the same and equal to 1. Later, McWeeny[278] showed that the formal charge on carbon can be represented as the sum of the local charge of the atom and the charge of the bond. It was concluded that two carbon atoms with equal formal charges can have different local charges, so that the distribution of the charges in alternant hydrocarbons may be unsymmetrical. Maslen and Coulson[279] calculated the charges of the atoms and bonds in linear polyenes (without allowance for the distribution of electrons in the σ-bonds). The following values were obtained for butadiene:

$$\overset{0.82}{C}\overset{}{=}\underset{0.35}{\overset{0.75}{C}}\overset{}{-}\underset{0.14}{\overset{0.75}{C}}\overset{}{=}\underset{0.35}{\overset{0.82}{C}}.$$

Thus the values of the π-electron charges on the $C_{(1)}$ and $C_{(4)}$ atoms are greater than those on the $C_{(2)}$ and $C_{(3)}$ central atoms. An interesting feature is that the charges on the $C_{(1)}$ and $C_{(4)}$ atoms almost coincide with the values of the charges on the carbon atoms in ethylene, calculated by the same authors[279]. The magnitude of the C=C moment, determined by Maslen and Coulson only on the basis of the non-equivalent distribution of the π-electron density along the bond, amounts to ~ 0.45 D.

Fukui and coworkers[280] used the LCAO MO-method to calculate the σ-electronic charges of the atoms in butadiene. The calculations gave the following σ-electron density distribution:

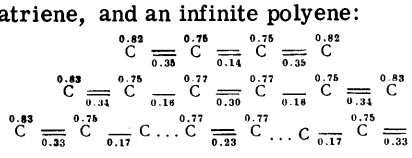
$$\overset{0.18}{C}=\overset{0.11}{C}-\overset{0.11}{C}=\overset{0.18}{C}.$$

The dipole moment of the C=C bond due to the non-equivalent distribution of the σ-electrons of butadiene amounts to ~ 0.45 D and is directed in the same direction.

Thus the data on the electron density distribution in butadiene obtained from quantum-mechanical calculations and analysis of the intensities of the infrared spectra show qualitative agreement.

The polar properties of conjugated compounds containing a larger number of units in the chain were studied by Ivanova, Lubuzh, and the present authors[252,253,255] using the intensities of the infrared absorption bands of $\alpha\omega$-substituted polyenes of the type $X-[CH=CH]_n-X$, where $X = COOC_2H_5$ and $n = 2-7$, and poly-ynes of the type $R-[C\equiv C]_n-R$, where R = Alk and $n = 2-4$. The experimental data on the intensities of the absorption bands of the polyenes at about 1600 cm^{-1} and of the poly-ynes at about 2200 cm^{-1}, and an analysis of the forms of the vibrations, indicate that the observed proportionate increases in the integral intensities of absorption for the polyenes and poly-ynes are due chiefly to the increase in the number of bonds taking part in the vibrations, and not to changes in the polar properties of the chains. Calculations of the intensities of the absorption bands of polyenes led to the conclusion that the values of the polarisation of both single and double bonds depend little on the position of the bonds in the chain. Good agreement between the experimental and calculated values of the relative intensities of the infrared absorption bands of the polyenes at about 1600 cm^{-1} was obtained with the assumption that the polarisation of a single bond is equal to half the polarisation of a double bond and of opposite sign. Thus studies of the frequencies of the normal vibrations and the intensities of the infrared absorption bands show that in molecules with alternating multiple and single carbon–carbon bonds there is alternation of both bond orders and charges on the carbon atoms along the chain, the degree of alternation in both instances being independent of chain length. Thus the frequencies and intensities of alternant hydrocarbons can be explained within the framework of a single model with partly delocalised bonds. Moreover, the data obtained cannot be explained using the hybridisation concept.

The conclusion, which follows from the analysis of the infrared spectra, that there is alternation of the charges on the carbon atoms in a polyene chain, agrees with the results of quantum-mechanical calculations by Maslen and Coulson[279]. The following results were obtained for butadiene, hexatriene, and an infinite polyene:



These data show that the charges on the atoms of the terminal bonds are independent of the dimensions of the polyene chain. The charges on the atoms of the central bonds in the polyenes also remain unchanged with increase in the number of units. The dipole moments of the double and single bonds have opposite directions. It may be noted that quantum-mechanical calculations and analysis of the infrared spectra lead to a polyene model in which the central bond has no dipole. Other data also point to a model in which the central bond exhibits unique properties. Even in long polyenes, the central bond exhibits specific chemical and stereochemical properties[148]. For example, of the large number of possible *cis–trans* isomers of a polyene chain, the one most readily realised is that with the central double bond in the *cis*-configuration. Ease of isomerisation at the central double bond is observed in the molecules of lycopene and the α-, β-, and γ-carotenes. The molecules undergo relatively easy rupture at this point[148].

As already noted, the force fields of conjugated nitriles differ qualitatively from the force fields of conjugated hydrocarbons. In particular, the force constants of the C=C, C≡C, and C≡N bonds and the intermediate C–C bonds in cyanoethylenes and cyanoacetylene (Table 3) have values which are close to the corresponding constants for the isolated multiple bonds and the simple σ-bond. Study of the intensities of the infrared absorption bands of acrylonitrile[281] showed that the mutual influence of the multiple carbon–carbon bonds and the nitrile group produces an electron density distribution which differs significantly both from that for simple molecules and from that for alternant hydrocarbons without leading to appreciable π-electron delocalisation. Calculation of the electro-optical parameters gives a dipole moment of ~ 1.0 D for the double bond in acrylonitrile with the negative charge on the $C_{(2)}$ atom, that is, the direction of the double bond moment in acrylonitrile is the opposite of that for butadiene and vinylacetylene. The double bonds in the C=C–C≡N and C=C–C≡C (or C=C–C=C) systems differ in the values of the π-orders, in the nature of the electron density distribution along the bond, in the ability of the charge to migrate during the vibration (this is much smaller for acrylonitrile than for vinylacetylene and butadiene). In these conjugated nitriles, the displacement of the electron density towards C≡N takes place chiefly within individual bonds. There may be instances when the inductive effect causes the electrons to leave the limits of their "own" bonds. This requires a relationship between the donor and acceptor properties of the interacting atomic groups which is different from that in acrylonitrile and cyanoacetylene. These conditions are satisfied, for example, in the cyanamide molecule, in which the inductive effect leads to delocalisation of the electrons of the unshared pairs of the nitrogen and a change in its valency state[282].

The electron density distribution in acrylonitrile was recently studied by Halper and coworkers[283] using the simple Hückel method with allowance for overlap. The results obtained show good agreement with the results of the analysis of the intensities of the infrared absorption bands. The dipole moment of the C=C bond, determined on the basis of the π-charges on the atoms found by Halper and coworkers[283], amounted to ~ 0.7 D, compared with the value of ~ 1.0 D obtained from the infrared spectra[281].

Study of the electron density distribution in butadiene, diacetylene, vinylacetylene, and polyenes and poly-ynes with higher molecular weights showed that the delocalisation of the electrons in these molecules leads to polarisation of the bonds. In molecules known to contain polarised bonds (cyanogen, cyanoacetylene, and cyanoethylenes), however, the delocalisation of the π-electrons is significantly smaller, and is probably due to different factors. As already noted, the direction of the displacement of the electron density of multiple bonds in these molecules under the influence of the inductive effect of the acceptor nitrile group is the opposite of that for the analogous bonds in compounds with purely carbon–carbon conjugation. Thus the effect of delocalisation and the inductive effect have opposite influences on the π-electron density distribution. It is probably because of this feature, and also because of the polarisation of the bonds on delocalisation and the production of an inductive interaction, that the alternation of the bonds is preserved in linear polyenes and poly-ynes. The degree of alternation, that is, the orders of the multiple and single bonds, is determined by the competition between the two effects. In aromatic compounds, for example, in benzene, the complete equalisation of the bonds is due to

the fact that π-electron delocalisation is possible whereas polarisation is impossible, that is, only one effect operates.

Let us now consider the Raman spectra of conjugated systems. The Raman spectra of the esters of polyene $\alpha\omega$-dicarboxylic acids $C_2H_5OOC[CH=CH]_nCOOC_2H_5$, where $n = 2-8$, and diphenylpolyenes $C_6H_5[CH=CH]_nC_6H_5$, where $n = 5$ or 6, were studied in detail by Shorygin and Ivanova[251,284,285]. It was found that with increase in n, the intensities of the various Raman lines of the polyenes do not increase to the same extent. In the spectra of short polyenes ($n = 2-4$) the number of observed lines assigned to the vibrations of the chain corresponds exactly to that predicted by theory for centrosymmetric molecules. With increase in n, the frequency of the exciting light approaches the range corresponding to the characteristic frequencies of the electronic transitions, and when the frequencies coincide, that is, with excitation in or close to the resonance range, not all of the Raman-active vibrations of the polyene chain are observed, but only two normal vibrations ($\sim$ 1600 cm^{-1} and 1140 cm^{-1}) and their overtones and combination frequencies (as far as the fourth order). An interesting feature is that the maximal deviations of the frequencies of higher order from the multiple fundamental tones, due to anharmonicity, are small and amount to $\sim$ 30 cm^{-1}. The lines at $\sim$ 1600 cm^{-1} and 1140 cm^{-1} are characterised by unusually high absolute intensities. Approximately the same frequencies are observed in the vibrational structure of the first absorption bands and fluorescence bands in a number of other polyenes[286]. These lines are also present in the Raman spectra of polyenes with various substituents in the α- and ω-positions[287]. With increase in the number of double bonds, the frequency in the region of 1600 cm^{-1} decreases regularly, approaching a definite limit, whereas the 1140 cm^{-1} frequency is independent of chain length. Calculations for polyenes[243,245] showed that this behaviour of the Raman frequencies is not due to equalisation of the bonds. The reason for the unique activity of the symmetric vibrations at $\sim$ 1600 cm^{-1} and 1140 cm^{-1} compared with the other vibrations permitted by symmetry for a system of conjugated double bonds is that only these vibrations involve the entire polyene chain, so that they are accompanied by the maximal change in the polarisability of the molecule.

The reason for the marked decrease in the frequencies at $\sim$ 1600 cm^{-1} with increase in the length of the chain ($\sim$ 100 cm^{-1} on going from $n = 2$ to $n = 8$) without change in the nature of the bonds and with preservation of the 1140 cm^{-1} frequency under the same conditions was investigated[281] by comparing the zeroth amplitudes of the double ($\bar{Q}$) and single ($\bar{q}$) bonds. It was found that the ratio $\bar{Q}/\bar{q}$ for the vibrations at $\sim$ 1600 cm^{-1} decreases with increase in the length of the chain, the decrease being greater for the first terms of the vinyl series, but remains almost constant for the vibrations at 1140 cm^{-1}. Since the overall change in the double and single bonds in these vibrations depends little on chain length, the decrease, with increase in n, in the relative participation of the more rigid double bonds in the $\sim$ 1600 cm^{-1} vibration leads to a decrease in the frequency without change in the nature of the bonds. With the condition that the ratio $\bar{Q}/\bar{q}$ is constant, the frequency at 1140 cm^{-1} can remain unchanged in the spectra of various polyenes only if the elastic properties of the bonds are preserved irrespective of chain length[288].

3. Transfer of Influence Along a Chain of Conjugated Bonds

The concept of molecules with alternating multiple and single carbon–carbon bonds as systems transferring the influence of substituents without significant weakening (vinylogy) is widely encountered in the literature. Analysis of the available data on the physical and chemical properties of conjugated compounds, however, indicates that there is little justification for these views. Thus calculations of the vibrations of linear polyenes and poly-ynes[243,245,255] showed that significant interaction takes place only between the closest multiple bonds. With increase in the number of intermediate units, the interaction rapidly becomes weaker and is almost imperceptible for multiple bonds separated by more than two carbon atoms. It is natural to assume that the mutual influence of substituents in the α- and ω-positions will decrease to the same extent. The problem of the transfer of influence through a system of conjugated bonds was examined by Ivanova and the present authors[243,253] in an analysis of the vibrational spectra of the esters of polyene $\alpha\omega$-dicarboxylic acids ($n = 2-8$), unsymmetrical polyenes $X-[CH=CH]_nCOOC_2H_5$ ($X = CH_3$, NO_2, and CHO, $n = 2-4$) and $\alpha\omega$-dinitriles $NC-[CH=CH]_n-CN$ ($n = 4$ or 5). The study showed that the values of the frequencies and intensities of the C=O stretching vibrations in the infrared spectra of the esters $C_2H_6OOC[CH=CH]_nCOOC_2H_5$ are independent of chain length and agree with the corresponding values for the $\alpha\beta$-unsaturated esters of carboxylic acids (RCH=CHCOOR, R = Alk[289]). Change in X and n in $X-[CH=CH]_nCOOC_2H_5$ did not lead to marked changes in the frequencies and intensities of the absorption bands of the carbonyl group in the spectra. This indicates that a conjugated system of carbon–carbon bonds in the ground electronic state of the molecule does not effectively transfer the influence of substituents. This conclusion is confirmed by the agreement shown by the ν_s and ν_{as} frequencies of the C=O vibrations in the spectra of polyene diesters and the C≡N vibrations in the spectra of polyene dinitriles. The absence of splitting of the frequencies of the symmetric and antisymmetric vibrations of equivalent atomic groups in the spectra of symmetrical molecules indicates the absence of mechanical and electronic interaction between the groups[290,291]. The conclusion that substituents at the ends of a polyene chain have an extremely restricted sphere of influence agrees with data obtained by Hutchinson and Sutton[179] on the dipole moments of the series of polyenes $(H_3C)_2N-[CH=CH]_n-CHO$ ($n = 0-4$) and data obtained by Yanovskaya[292] on the ionisation constants of polyene mono- and di-carboxylic acids. The nature of the changes in both dipole moments and ionisation constants with increase in chain length shows that the mutual influence of substituents separated by a conjugated chain weakens very rapidly. It can hardly be detected by dielectric or potentiometric measurements or by vibrational spectroscopy even for polyenes with $n \geq 3$. Quenching of the influence of substituents was also observed by Shorygin and Ivanova[293,294] from the Raman spectra of various other classes of conjugated compound. A long system of conjugated bonds does not transfer the influence effectively even when one end of the chain carries a substituent with clearly defined electron-donating properties (for example, R_2N-) and the other carries a substituent with clearly defined electron-accepting properties ($-NO_2$).

4. Classification of the Force Fields and Electric Fields of Organic Compounds

A considerable amount of material on the force fields of various classes of organic compound has now accumulated. Its analysis has enabled the present authors[266] to classify

force fields (initially on the basis of purely external characteristics) into several types, arbitrarily described as non-conjugated, aromatic, mesomeric, and inductive. It was found that this classification corresponds to the electronic structures of the molecules. Each type of force field is determined by a definite form of electron density distribution. The force constants of bonds and their interaction constants for simple molecules are given in Table 3.

We have already noted the characteristic features of the force fields of saturated hydrocarbons, compounds with isolated multiple bonds, aromatic compounds, and linear polyenes and poly-ynes. The force fields of conjugated molecules containing electron-accepting groups exhibit certain specific features. The data given above for the molecules of acrylonitrile and cyanoacetylene show that the polarisation of multiple carbon–carbon bonds has little influence on the values of the diagonal elements, but leads to an increase in the non-diagonal elements of the interaction of the bonds.

The sets of force constants of each type describe the vibrational spectra of a large number of molecules with the corresponding electron density distribution. The force constants of the non-conjugated type describe the spectra of alkanes, alkenes, and alkynes; those of the aromatic type describe the spectra of benzene derivatives and condensed aromatic compounds; those of the mesomeric type describe the spectra of polyenes, poly-ynes, and vinylacetylenes; and those of the inductive type describe the spectra of a large number of nitriles[295,264,265]. Each type of force field is characterised by definite values of the force constants of the bonds and values of the bond interaction constants. Changes in the constants are mutually related. Thus decrease in the constants of the multiple bonds in linear polyenes and poly-ynes (as a result of π-electron delocalisation) is accompanied by an increase in the constants of the single bonds and the bond interaction constants (as a result of the formation of multi-centre orbitals). Change in the nature of the electron density distribution leads to a change in the complete set of force constants. Within a given type of force field, however, the values of the constants are transferable.

The classification of force fields facilitates the solution of two problems. When the force field is known, its classification in a given type immediately gives information on the electronic structure of the molecule. On the other hand, a knowledge of merely the nature of the electron density distribution in a molecule increases considerably the reliability of the determination of force constants. The existence of a correlation between the structure and force field of a molecule imposes a number of additional conditions on the solution of the reverse spectroscopic problem. An example is provided by the study of the molecules of cyclo-octatetraene (C_8H_8) and butatriene (C_4H_4).[286] The frequencies of the vibrations of these extremely complex molecules were determined using force fields compiled on the basis of data on their electron density distributions. Calculations of the normal vibrations for C_8H_8 and C_8D_8, in agreement with quantum-mechanical calculations[24], confirmed that there is no significant π-electron delocalisation in cyclo-octatetraene, despite the formal resemblance to the molecules of alternant hydrocarbons. In the calculation for butatriene it was assumed that the nature of the electron distribution in one of the planes of the molecule is similar to that in butadiene, and in the other (perpendicular to the first) is similar to that in an isolated double bond. In accordance with this assumption, the force field of butadiene was compiled by superimposing fields of two types—mesomeric and non-conjugated. In the determination of the numerical values of the force constants, the values of the orders of cumulative bonds for butatriene obtained by the MO method[221] were assumed, and use was made of the relationship between the force constant, hybridisation type, and bond order (Figs. 7 and 8). The frequencies of the vibrations of butatriene calculated for these conditions showed good agreement with the observed values. Recently, an attempt was made to calculate, on the basis of the proposed classification of force fields, the frequencies of the vibrations of vinylacetylene and the four methyl derivatives of vinylacetylene using constants selected on the basis of definite assumptions regarding the electron density distribution in the C=C–C≡C system[259]. Agreement between all the calculated and experimental frequencies (more than 120) was obtained only when a force field of the mesomeric type was used. It should be borne in mind, however, that the proposed classification[266] of force fields is to some extent arbitrary. A sharp distinction cannot be made between the force fields of organic molecules, particularly molecules containing hetero-atoms. When there is strong intramolecular interaction between individual atomic groups, the force field of the molecule may appear in a new form or exhibit the features of several types simultaneously. Examples are provided by the molecules of $\alpha\beta$-unsaturated ketones[296] and the cyanamide molecule[282]. Nevertheless, a knowledge of the force fields of the limiting structures is also necessary in complicated cases.

A much more complete picture of the electronic structure of a molecule in the ground state can be obtained by simultaneous analysis of the force field and the electric field. Data are now available on the electric fields of a comparatively large number of molecules of organic compounds of various classes[256,275,281,297-304]. These values were obtained with the same approximation and within the framework of a single calculation scheme by Gribov[274]. Calculations showed that the electro-optical parameters characterise the properties of only the electron cloud of the molecule and in this sense they resemble force constants. A paper by one of the present authors[305] classified the electric fields of organic molecules and established a correlation between the specific features of the electronic structure and the characteristic features of the electric field.

Calculation of the intensities of the infrared absorption bands of saturated hydrocarbons and compounds with isolated multiple bonds[256,298-301] showed that the electro-optical parameters of the $-CH_3$, $=CH_2$, and $\equiv CH$ groups, found for simple molecules, can be used to describe satisfactorily the intensities for more complex alkane, alkene, and alkyne molecules. Thus within a series of these compounds, the electro-optical parameters of the above groups, like their force constants, are transferable. The mechanical and polar properties of the $-CH_3$, $=CH_2$, and $\equiv CH$ groups in the molecules of a given series remain to a considerable extent unchanged, that is, the electron density distribution remains approximately the same. The electric fields of alkanes, alkenes, and alkynes are also characterised by low values for the dipole moments and polarisations of the carbon–carbon bonds. The participation of purely carbon-carbon bonds in the vibrations of the molecules does not make a significant contribution to the intensities of the infrared absorption bands. This leads to the at first sight paradoxical conclusion that the infrared spectra of compounds of these classes are due chiefly to the electro-optical properties of the CH bonds.

The electric fields of linear conjugated molecules belong to a different type. Butadiene[275], diacetylene[276], and vinylacetylene[276], as well as polyenes[252] and poly-ynes[255]

with higher molecular weights are characterised by appreciable dipole moments and polarisations of the carbon–carbon bonds. In the C=C–C=C, C=C–C≡C, and C≡C–C≡C systems the excess of negative charge is found on the $C_{(1)}$ and $C_{(4)}$ atoms. The electro-optical parameters of identical atomic groups in the molecules of conjugated hydrocarbons have similar values. Thus the electric field of vinylacetylene can be made up almost entirely of the parameters of the corresponding atomic groups of butadiene and diacetylene[276,305], and the electric fields of polyenes can be made up of the parameters of butadiene[252]. In this sense the electro-optical parameters of butadiene and diacetylene are transferable and can be used to compile the electric fields of more complex linear molecules with alternating multiple and single carbon–carbon bonds. It was noted above that in the same series of compounds an analogous property is shown by the force constants of butadiene and diacetylene. Thus for conjugated molecules, as for non-conjugated molecules, the transferability of some parameters is accompanied by the transferability of others. A correlation between electric fields and force fields is also observed for the molecules of other classes of organic compound. In all cases each type of electric field corresponds to a definite type of force field.

The results of experimental and theoretical studies of conjugated hydrocarbons enable the following conclusions to be reached regarding their structures and certain other properties.

1. Linear polyenes and poly-ynes consist of systems of conjugated alternating bonds. Increase in the length of the chain does not lead to appreciable equalisation of the carbon–carbon bonds. The lengths and orders of the multiple and single bonds in polyenes and poly-ynes with high molecular weights are approximately the same as those for butadiene and diacetylene respectively.

2. Organic dyes (polymethines, cyanines, and oxonols) contain equalised bonds. With increase in the length of the chain, the lengths and orders of the bonds approach those of the bonds in benzene.

3. Cumulenes consist of systems of double bonds conjugated in two mutually perpendicular planes; increase in the length of the chain does not lead to a change in the lengths and orders of the bonds. In a cumulene with a long chain, all the bonds except the terminal bonds have the same lengths and orders. As for other compounds with equalised bonds, λ_{max} in the ultraviolet spectra of the cumulenes is displaced by a constant amount with the addition of each new unit.

4. The lengths and energies of carbon–carbon bonds are not equally sensitive to bond order throughout the entire range of possible change in this quantity. Preservation of the lengths and energies of the bonds of a given hybridisation type in the molecules of organic compounds cannot be taken as a basis for rejecting π-electron delocalisation.

5. Delocalisation of π-electrons and the associated changes in the orders of multiple and single bonds does not lead to a significant change in the lengths and energies of the bonds in polyenes and poly-ynes. The increase in the energy and the decrease in the length of the single bonds in alternant hydrocarbons are determined chiefly by the valency state of the carbon atoms.

6. The lengths and energies of the bonds in polymethines, cyanines, oxonols, and aromatic compounds depend almost exclusively on the bond orders, the corresponding relationships being almost linear.

7. Delocalisation of π-electrons in polyenes and poly-ynes leads to a non-equivalent distribution of electron density along each bond, with the exception of the central bond. In butadiene, vinylacetylene, and diacetylene, the positive ends of the dipoles of the multiple bonds are the central carbon atoms. With increase in the length of the chain, alternation of the bond orders, and also alternation of the charges on the atoms, are preserved.

8. The mutual influence of atomic groups separated by a chain of conjugated carbon–carbon bonds rapidly becomes weaker with increase in the number of intermediate units.

9. The characteristic features of the force fields and electric fields of conjugated hydrocarbons are determined chiefly by π-electron delocalisation.

10. The methods of quantum chemistry and vibrational spectroscopy lead to the same picture of the structure of conjugated hydrocarbons.

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A number of interesting experimental and theoretical papers on the structures of conjugated hydrocarbons appeared after the present manuscript had been submitted for publication. We can now only mention briefly some of these papers, most directly related to the topics discussed above.

Page 121. Traetteberg[306] has made a new study of the structure of cyclo-octatetraene. The value which he obtained for the C–C bond length in this molecule (1.475 Å) is greater than the value found earlier (1.460 Å)[23]; there is now almost no difference between the length of this bond and the length of the single carbon–carbon bond in butadiene.

Page 126. Studies confirming the alternation of the charges on the atoms and the bond orders in polyenes now include the following: calculations by Flurry and Bell[307] using the SCF MO LCAO method in the Pariser–Parr–Pople approximation, including resonance integrals characterising non-neighbouring interactions; calculations by Misurkin and Ovchinnikov[308] using the Hartree–Fock generalised self-consistent field method; calculations for $\alpha\omega$-diphenylpolyenes using Pariser–Parr–Pople method; calculations for polyenes by Adams and Miller[310] using a modified method with self-consistency; calculations for dienes and hexatriene by Allinger and coworkers[311] using the Pariser–Parr method; and calculations for polyenes by Kutzelnigg[312] within the framework of the simple Hückel approximation using a perturbation method.

Alternation of bond lengths was obtained by Haugen and Traetteberg[313] in an electron-diffraction study of 1,3-butadiene ($L_{C=C}$ = 1.343 Å and L_{C-C} = 1.467 Å) and *trans*-1,3,5-hexatriene ($L_{C=C}$ = 1.345 Å and L_{C-C} = 1.450 Å).

Page 127. Dähne and Leupold[314] published a review on the calculation of the electronic spectra of dyes of various classes.

Page 132. Cherniak and Costain[315] showed by microwave spectroscopy that the lengths of the C–C bonds in *trans*-acrolein and 1,3-butadiene are approximately equal (1.470 Å).

Page 134. Data indicating non-equivalent distribution of the π-electron density along the carbon framework of 1,3-butadiene were obtained by Hobgood and Goldstein[316] in an analysis of the NMR spectra.

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The Masking of Reactions

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CONTENTS

I.	Introduction	142
II.	Classification of masking processes	143
III.	Methods for calculating the efficiency of masking	144
IV.	Masking and the selectivity of reactions	148
V.	The most common masking agents	149
VI.	Characteristic examples of the practical application of masking	153

I. INTRODUCTION

Any chemical reaction is characterised not only by stoichiometric conditions but also by thermodynamic and kinetic conditions. Changes in the last two conditions may increase the rate of a reaction or, on the other hand, decrease the rate of the reaction until the reaction is completely suppressed. In recent years the rapid development of science and technology has faced chemists with a number of problems associated with the suppression of undesirable chemical processes[1], and the attention of chemists is now drawn equally to problems of increasing reaction rates and problems of decreasing reaction rates.

One particular example of the retardation of chemical reactions is masking, which is of considerable importance in analytical chemistry. The term masking is used to describe the retardation or complete suppression of a reaction in the presence of substances capable of altering the rate or direction of the reaction as a result of their influence on its kinetic or thermodynamic conditions without the physical or chemical separation of the participants of the reaction into a new phase. The substances introduced into the reaction medium in order to retard or suppress the reaction are called masking agents. A classical example of the masking of a reaction is the non-precipitation of $Fe(OH)_3$ from an alkaline solution containing F^- ions; in this example, F^- prevents the formation of $Fe(OH)_3$, by combining with Fe^{3+} to form the soluble complex FeF_6^{3-} (that is, by bringing about another, thermodynamically more favourable reaction) and thus acts as a masking agent for the reaction of Fe^{3+} with OH^-.

Frequently, instead of the masking of a reaction, one speaks of the masking of the ions (or molecules) taking part in the reaction; usually it is not even emphasised which of the ions taking part in the reaction being masked are in fact masked directly, that is, which of the ions is responsible for the masking of the reaction as a whole. For example, in the masking of the formation of the yellow molybdophosphate complex in the presence of $C_2O_4^{2-}$ in the traditional use of this masking agent to eliminate the interfering influence of PO_4^{3-} in the photometric determination of Si, reference is made to the masking of the PO_4^{3-} ion, rather than to the masking of the MoO_4^{2-} ion, although it is the MoO_4^{2-} ion which is responsible for the masking of the reaction, since it reacts with $C_2O_4^{2-}$ to form a colourless soluble complex. In most instances when a knowledge of the mechanism of masking is not required, this replacement of concepts, with a correct understanding of the essential features of the process, is quite justified, but for greater accuracy and to avoid misunderstanding it is desirable even in these instances to indicate the reaction (or reagent) with respect to which a given ion is masked. The statement (without any additional information) that a given ion is masked should evidently be understood to mean that all the reactions which are possible for this ion in the given reaction medium (before the addition of the masking agent) are masked. Thus if one speaks of the masking of Fe^{3+} by tartrate in the determination of Ni by dimethylglyoxime, one means that the Fe^{3+} is masked with respect to all reactions possible for this ion under the conditions of the determination of Ni, including (and this is the most important) the formation of $Fe(OH)_3$.

Frequently, the masking of ions is erroneously identified with the separation of ions, and it is forgotten that the separation of ions, unlike masking, always involves the transfer of ions into a new phase, that is, their actual removal from the sphere of reaction. For example, the reaction of NH_4^+ with CH_2O with the formation of soluble hexamethylenetetramine $(CH_2)_6N_4$ is a typical example of masking of the NH_4^+ ion, but the decomposition of NH_4^+ by nitrite with the formation of the gaseous product N_2 cannot be regarded as masking of the NH_4^+ ion. According to the same principle, masking does not include examples where the interfering influence of ions is eliminated by precipitating them in the form of sparingly soluble compounds, even when the latter remain in the mother-liquor [for example, the precipitation of Mg^{2+} as $Mg(OH)_2$ in the complexometric titration of Ca^{2+}].

The incorrect view that masking is merely a method for eliminating the interfering influence of substances in qualitative and quantitative analysis is widely encountered. Masking is a process in which the ion or molecule being masked, under the influence of the masking agent, loses its ability to undergo certain reactions characteristic of the ion or molecule. Like any other process, masking may be either desirable or undesirable, that is, it may be useful or harmful. Thus the masking of many qualitative reactions of the cations of analytical groups II and III in the presence of PO_4^{3-} is undesirable and steps have to be taken to prevent it. On the other hand, the masking of accompanying ions in various analytical reactions is useful and desirable, and is used to eliminate the interfering influence of these ions.

Masking has two significant advantages over methods of separation as a method for eliminating the interfering influence of substances: maximal speed, since almost no time is required for the actual masking, and high efficiency due to the absence of the usual errors associated with phase separations. Because of these advantages, the masking of reactions and ions has now become an extremely widespread and powerful means of eliminating the interfering influence of the medium in chemical analysis. This

has been greatly facilitated by the work of Feigl[2,3], who first drew attention to the importance of the study of the masking of reactions and ions in analytical chemistry, and also by Ringbom[4-6], Reilley and Schmid[7], Suzuki[8,9], Tanaka[10,11], Chaberek and Martell[12], Cheng[13], Schwarzenbach[14], and Yatsimirskii[15,16], who have made important contributions to the theory of masking processes.

Although the study of problems in the theory and practical application of masking is not restricted to analytical chemistry, but is also of importance in, for example, biology, and various branches of industry[12], the present state of development of these problems is closely related to the development of general problems in analytical chemistry. The present paper therefore deals chiefly with analytical aspects of the masking of reactions and ions.

II. CLASSIFICATION OF MASKING PROCESSES

Two basic types of masking can be distinguished, according to their fundamental nature: (1) masking due to a change in the thermodynamic conditions for the reaction being masked; and (2) masking due to a change in the kinetic conditions for the reaction being masked.

In all examples of masking belonging to the first type, the essential feature of the masking action of the substances specially introduced (or the factors deliberately altered) is the change in the reaction system from the initial equilibrium state in the newly created conditions; a characteristic feature of this new equilibrium state is that the reaction being masked takes place to the minimal extent. This type of masking can be described as equilibrium (or thermodynamic) masking. In equilibrium masking, the masking action responsible for the change in the direction of the reaction being masked is described qualitatively by le Châtelier's principle, and quantitatively by the corresponding thermodynamic equations, in particular the equation for the law of mass action (when there is a change in the concentration of the substances taking part in the reaction being masked) and the isobar or isochore equations (when there is a change in temperature).

In specific instances, masking action of the first type is brought about by the most varied mechanisms: (a) mechanical introduction of additional quantities of the compound which is the product of the reaction being masked; (b) oxidation or reduction of one or more of the substances taking part in the reaction being masked; (c) the reaction of one or more of the participants in the reaction being masked to form soluble complexes (including chelate compounds); and (d) the reaction of one or more of the participants in the reaction being masked to form other types of soluble compound (molecular adducts, ion associates, covalent compounds, etc.). This list should also include the masking of reactions as a result of a change in temperature and pressure (without the introduction of special masking agents) and also as a result of a change in the composition of the reaction medium (the nature of the solvent, ionic strength, etc.). In the last instance, and also when the direction of the reaction being masked is changed as a result of the addition of an excess of the product of the reaction, the original form of the substances being masked remains unchanged.

The following are some examples: (a) in the cerimetric titration of Fe^{2+}, Sn^{2+}, or Sb^{3+}, the interfering reaction between AsO_2^- and Ce^{4+} can be reliably masked with a large excess of AsO_4^{3-}, which is the product of the reaction of AsO_2^- and Ce^{4+}; (b) in the hydrogen sulphide scheme of qualitative analysis, $Cr_2O_7^{2-}$ is masked by reduction to Cr^{3+} with ethanol; (c) the oxidising reactions of Fe^{3+} are completely masked in the presence of ethylenediaminetetraacetate (EDTA), which combines with Fe^{3+} to form a stable soluble complex; and (d) in the titrimetric analysis of mixtures of H_2SO_3 and HSO_3^-, the acid strengths of these substances are "moved apart" by masking the HSO_3^- with formaldehyde, which reacts with HSO_3^- to form a soluble adduct with stability constant $\sim 10^7$.

The basis of masking action of the second type is the kinetic effect: the masking agent introduced into the reaction medium decreases the rate of the reaction being masked, either directly or by removing one of the participants of the reaction being masked, in another, more rapid reaction. In this instance the masking is not associated with the attainment of stable thermodynamic equilibrium in the system; this distinguishes the second type of masking from the first type, and the second type of masking can be described briefly as non-equilibrium (or kinetic) masking. The masking action produced by the kinetic effect can in principle be described quantitatively by the appropriate kinetic equations.

Comparatively few examples of masking of the second type have been studied (and hence become familiar), although this does not mean that they are not widely encountered. The primary example is masking based on negative catalysis, when the presence of a masking agent (which in this instance plays the part of catalyst) excludes one of the reaction paths which is possible in its absence, leaving slower reaction paths unaffected. An example of catalytic masking is provided by the suppression of the oxidation of AsO_2^- by $Cr_2O_7^{2-}$ ions in the presence of Mn^{2+} in the dichromate titration of Fe^{2+} (Mn^{2+} acts as negative catalyst for the spontaneous reaction of AsO_2^- with $Cr_2O_7^{2-}$). The action of the catalyst masking agent on the reaction being masked involves its intermediate chemical reaction with the reacting substances with the restoration of the original forms of these substances after each cycle of the intermediate reactions; the substances being masked thus remain finally unchanged.

A form of masking which is very similar to catalytic masking is that involving the suppression of induced (conjugated) reactions. The mechanism of the masking action in this instance has its own characteristic features, associated with the differences between induced reactions and purely catalytic reactions, and it makes allowance for the stoichiometry of the induction and the irreversible chemical transformation of the inductor, but, as in the previous example, the substances being masked retain their original forms as a result of the masking. A familiar example of the masking of an induced reaction is the suppression of the oxidation of Cl^- in the permanganometric titration of Fe^{2+} in the presence of Mn^{2+}, which acts as masking agent for the Cl^- ion.

Finally, the second type includes masking based on the difference in the rates of the reaction being masked and the masking reaction with a common participant—the masking agent. This principle forms the basis, for example, of the complexometric titration of Fe^{3+} in the presence of Cr^{3+}, which, unlike Fe^{3+}, forms a soluble complex with EDTA only very slowly, although the stability constants of the complexonato-compounds of Fe^{III} and Cr^{III} are close to one another (10^{25} and 10^{23} respectively); in this example, EDTA acts simultaneously as complexometric titrant for Fe^{3+} and masking agent for Cr^{3+}.

The above general and fundamental classification of masking processes naturally provides for special classifications of importance in various particular instances.

Thus if the masking of ions is one of the stages in the analysis of complex mixtures, it is usually always followed by demasking of the ions; in these instances the selection of rational methods of demasking is facilitated by Suzuki's classification[8,9], based on the state of the ion after masking.

When we are dealing with the masking of individual ions (and not reactions), it is sometimes convenient to distinguish various forms (or techniques) of masking, for example, direct and indirect, single-stage and multi-stage, etc. The suppression of the reaction between PO_4^{2-} and MoO_4^{2-} in the presence of $C_2O_4^{2-}$ is an example of direct masking for MoO_4^{2-} and of indirect masking for PO_4^{3-} (most examples of equilibrium masking can be regarded in this way). The masking of the Cu^{2+} ion by glycerol (which forms a soluble complex with Cu^{2+}) in the qualitative analysis of the cations of analytical group IV is an example of single-stage masking, whereas the masking of the same Cu^{2+} ion by cyanide is an example of double (two-stage) masking, since in this example the Cu^{2+} is first reduced by the cyanide to Cu^{+}, after which it reacts with cyanide to form the soluble complex $Cu(CN)_4^{3-}$, that is, it is masked twice.

Special attention must be made of self-masking and buffer masking. The self-masking of a reaction is masking brought about by the reaction being masked; in this instance the addition of a special masking agent is not required, since its part is played by one of the reacting substances or reaction products (an example in the suppression of the formation of sparingly soluble HgI_2 at high I^- concentrations as a result of the formation of the soluble complex HgI_4^{2-}). Buffer masking differs from ordinary masking in that the substance added to the reaction medium is not the free masking agent but its complex with a given ion; the absence of a large quantity of free masking agent from the reaction medium leads to the strictly selective masking of only that reaction which is capable of being influenced by the very small quantities of masking agent produced by dissociation of the added complex. An example of buffer masking is the masking of Sr^{2+} by a mixture of EDTA and Mg^{2+} in the precipitation of Ba^{2+} as $BaCrO_4$ (the comparatively unstable complex of Mg^{2+} with EDTA formed in this instance does not prevent the quantitative precipitation of $BaCrO_4$, but is capable of creating conditions leading to the complete conversion of Sr^{2+} into a soluble complexonate).

III. METHODS FOR CALCULATING THE EFFICIENCY OF MASKING

1. The Masking of Reactions and Their Conditional Constants

For equilibrium (thermodynamic) masking, that is, for most examples of masking known at present, all the information on the masking process could in principle be obtained by solving the thermodynamic equations for the masked and masking reactions in the given system, containing the ions being masked and the masking agent. For systems of any complexity, however, this involves practically unsurmountable difficulties, since the necessary equilibrium constants are not known. This makes it necessary to examine the masking of reactions using approximate methods of calculation, and in some instances using semi-quantitative and qualitative-descriptive methods.

In analytical chemistry at present, ordinary (thermodynamic) equilibrium constants are being widely replaced by so-called "conditional constants", which were introduced by Ringbom[4,5] and which make allowance for the influence, on the main reaction, of all side-reactions possible in the given system (the reactions of the participants in the main reaction with hydrogen and hydroxide ions, buffer and masking agents, competing ions, etc.).

For a reaction of the type

$$M + A \rightleftarrows MA$$

the conditional constant is defined by the expression

$$K_{M'A'} = \frac{[MA]}{[M'][A']}, \quad (1)$$

where $[M']$ denotes the concentration of not only the free participant in the reaction M, but also all the M in solution which has not reacted with A. Similarly $[A']$ denotes the concentration of not only free A but also all the A which has not reacted with M.

The conditional constant for the reaction $K_{M'A'}$ is related to the ordinary equilibrium constant for this reaction K_{MA} by the simple relationship

$$K_{M'A'} = \frac{K_{MA}}{\alpha_M \alpha_A}, \quad (2)$$

where α_M and α_A are the so-called "α-coefficients" or "side reaction coefficients" proposed by Schwarzenbach[14]. For the reaction being considered, the α-coefficients are defined as follows:

$$\alpha_M = \frac{[M']}{[M]} \quad (3) \text{ and } \alpha_A = \frac{[A']}{[A]} \quad (4)$$

where [M] and [A] are the concentrations of free (not combined with one another or with other substances) participants in the reaction M and A respectively.

The α-coefficients α_M and α_A are functions of the equilibrium constants of the corresponding side-reactions. If, for example, one of the participants in the main reaction M (a metal ion) takes part in a side-reaction with a ligand L with the formation of a series of mononuclear complexes, we have

$$\alpha_{M(L)} = \frac{[M']}{[M]} = \frac{[M] + [ML] + [ML_2] + \ldots + [ML_n]}{[M]}, \quad (5)$$

or

$$\alpha_{M(L)} = 1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n, \quad (6)$$

where $\beta_1, \beta_2, \ldots \beta_n$ are the cumulative stability constants of the complexes of M with L. Similarly, if the second participant in the main reaction A (an anion) reacts with another cation N to form a series of complexes, we have

$$\alpha_{A(N)} = \frac{[A']}{[A]} = \frac{[A] + [NA] + [N_2A] + \ldots + [N_mA]}{[A]}, \quad (7)$$

or

$$\alpha_{A(N)} = 1 + \beta_1[N] + \beta_2[N]^2 + \ldots + \beta_m[N]^m, \quad (8)$$

where $\beta_1, \beta_2, \ldots \beta_m$ are the cumulative stability constants of the complexes of A with N.

In the above particular cases, when the side-reactions involve complex formation, the function giving the α-coefficients in terms of the equilibrium constants of the side-reactions is often called the degree of complex formation, following Yatsimirskii's suggestion[17].

Thus the α-coefficients essentially provide a quantitative measure of the extent to which side-reactions take place in the given system: in the absence of side-reactions, when M reacts only with A, $\alpha_M = 1$ and $\alpha_A = 1$; if, however, M and A take part in side-reactions with L and N respectively, $\alpha_{M(L)} > 1$ and $\alpha_{A(N)} > 1$.

The values of the α-coefficients for any ion can be calculated from the equilibrium constants of the corresponding side-reactions using equations of type (6) and (8), or determined experimentally by potentiometric, polarographic, or spectrophotometric methods, without using the equilibrium constants. The possibility of direct experimental determination of the α-coefficients, combined with the possibility of using the conditional constants in the same way as ordinary equilibrium constants, makes the principle of conditional constants of practical importance in the examination of various analytical problems, in particular the problems of masking action.

The principle of conditional constants is used in all known methods for calculating the efficiency of masking reactions, of which the most commonly encountered are the method which is referred to as the method of conditional constants, and the chelate buffer method.

2. Method of Conditional Constants

In the method of conditional constants, developed by Ringbom[4-6], the masking reactions are regarded as side-reactions with respect to the reaction being masked, so that the latter is taken as the main reaction in the given system. Accordingly, the masking of the reaction can be defined as a process (or technique) leading to a decrease in the conditional constant of this reaction.

Eqn. (2), which can be written in the more general form

$$K_{M'_mA'_n} = \frac{K_{M_mA_n}}{\alpha_M^m \alpha_A^n}, \qquad (9)$$

is the fundamental equation for the quantitative characterisation of masking action in various examples of equilibrium masking. The α-coefficients, which appear in this equation, provide a quantitative measure of the extent to which the masking reactions take place in the given system: in the absence of masking reactions, $\alpha_M = 1$ and $\alpha_A = 1$, but if M and A take part in masking reactions with the masking agents L and N, we have $\alpha_{M(L)} > 1$ and $\alpha_{A(N)} > 1$. In other words, the α-coefficients characterise the ability of ions to be masked by given masking agents (or the ability of the masking agents to mask the given ions), and the conditional constant defines the actual degree of masking of the reaction between these ions in the presence of the corresponding masking agents.

The problem of the value to which the conditional constant of a reaction must be reduced for the reaction to be regarded as masked is of practical importance; this value depends on the concentration conditions and on the degree of masking required. In complexometry, for example, the following limits are acceptable in most instances for the conditional constants of the reactions being masked: for $K_{M'A'} < 10^2$ the interfering reaction is almost completely masked, for $K_{M'A'} > 10^7$ there is almost no masking, and for intermediate values of $K_{M'A'}$ masking is incomplete.

The no less important problem of selecting a suitable masking agent is related to the calculation or determination of the α-coefficients. Eqn. (6) for the calculation of $\alpha_{M(L)}$, in addition to the cumulative stability constants of the complexes of M with L, contains the concentration of free masking agent [L]. If the analytical (total) concentration of L in the solution is much greater than the analytical concentration of the free metal ion M (that is, if $C_L \gg C_M$ and the dissociation of the complex ML is slight), masking of the reactions is observed in practice in most instances, and if L is the anion of a strong acid or of a weak acid which is completely dissociated at the given pH, we have

$$[L] = [L'] \simeq C_L - C_M \text{ (or even) } [L] \simeq C_L) \qquad (10)$$

If, however, L is a weak acid [L] in the general case is given by the equation

$$[L] = \frac{[L']}{\alpha_{L(H)}} = \frac{C_L - C_M}{1 + \frac{[H^+]}{K_m} + \frac{[H^+]^2}{K_m K_{m-1}} + \dots \frac{[H^+]^m}{K_m K_{m-1} \dots K_2 K_1}}, \qquad (11)$$

where $\alpha_{L(H)}$ is the coefficient of the side-reaction of L with H^+, and $K_1, K_2, \dots K_m$ the consecutive dissociation constants of the product of this reaction H_mL. In some instances, particularly for the ions of multivalent metals in strongly alkaline solutions, it is also necessary, in the calculation of the α-coefficients, to make allowance for the possibility of the reaction of M with OH^- with the formation of hydroxo-complexes; this can be done by introducing an additional side-reaction coefficient $\alpha_{M(OH)}$.

The calculation of the α-coefficients using Eqns. (6) and (8) is in general fairly tedious; it is therefore simpler and more convenient to use available α-coefficient values, which are usually provided in the form of graphs and tables. A collection of the values of the α-coefficients for a large number of ligands and metal ions is given in Ringbom's monograph[5]. Table 1 gives as an example the values of

Table 1. Logarithmic values of α_M (EDTA) (concentration of metal ion and EDTA 0.1 M; ionic strength $I = 0.5$).

Metal ion	pH														
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ag^+					0.1	0.5	1.5	2,6	3.7	4.7	5.5	5.9	6.0	6.0	6.0
Al^{3+}			1.8	4,1	6,2	8.2	10.3	12.5	14.5	16 5	18.3	21.3	25 3	29,3	33,3
Ba^{2+}							1.8	3.2	4.2	5.2	6.0	6.2	6.3	6.3	6.3
Be^{3+}					0.1	1.6	3.3	4,7	5.7	6,7	7,5	7.7	7,8	7,8	7.8
Ca^{2+}				0.1	1.1	3.2	4,7	6,1	7.1	8.1	8.9	9,1	9.2	9,2	9.2
Cd^{2+}		0.3	2.7	4.8	6.8	8.8	10.5	11,9	12.9	13.9	14.7	14,9	15 0	15.0	15.0
Co^{2+}		C.2	2.6	4.7	6.6	8.6	10.3	11.7	12.7	13.7	14.5	14.7	14.8	14.8	14.8
Cu^{2+}		1.9	4.6	6.8	8.7	10.7	12.5	13.9	15.0	16.0	16.8	17.3	18.0	18.9	19.9
Fe^{2+}			0.6	2.6	4.6	6.6	8.3	9.7	10.7	11.7	12.5	12.7	12.8	12,8	12.8
Fe^{3+}	3.8	7.0	10.3	13.0	15.2	13.2	18.9	20 4	22.0	24.0	26.4	28,5	30.6	32.6	34.6
Hg^{2+}	2.4	5.4	8.1	10.2	12.1	14.1	15.8	17.2	18.2	19.5	21 0	22.2	23.3	24.3	25.3
La^{3+}			0.8	3.5	5.7	7.7	9,4	10.8	11.8	12.8	13.6	13,8	13.9	13.9	13.9
Mg^{2+}						0.7	2,4	3.8	4.9	5,8	6.7	7.1	7.2	7.2	7.2
Mn^{2+}			0.5	2.4	4.3	6.3	8.0	9.4	10.4	11.4	12.2	12.4	12,4	12.4	12.4
Ni^{2+}	0.1	2.4	5.1	7.1	2.0	10.9	12.6	14.0	15.0	16.0	16.8	17.0	17.1	117.1	17.1
Pb^{2+}		1.4	4.2	6.3	8.2	10.2	12.0	12.4	14,4	15.4	16.2	16.4	16.5	116.5	16.5
Sr^{2+}					0.1	1.0	2.6	4,0	5.0	6.0	6.8	7.0	7,1	7.1	7.1
Th^{4+}	0.5	4.3	8.0	10.8	13.0	15.0	16.7	18,5	20.2	22,2	24,0	25,2	26.3	27,3	28.3
Zn^{2+}		0.3	2.8	4.9	6.8	8.8	10.5	11,9	12,9	13 9	14.7	14.9	15.0	15,0	15.6

the α-coefficients, taken from this monograph, for the most widely encountered masking agent EDTA, relative to the ions of various metals at various pH, and Table 2 gives the α-coefficients for the complexing anions most frequently used as masking agents, at various pH.

3. The Chelate Buffer Method

The chelate buffer method, developed by Chaberek and Martell[12] and Tanaka[10,11], is based on the recognition that a buffer action is produced in solutions containing a metal ion and ligand; when the system contains an excess of ligand, the metal ion is buffered (pM buffer), and in an excess of metal ion the ligand is buffered (pL buffer).

For the simplest system consisting of a metal ion M with total concentration C_M and an excess of ligand L with total concentration C_L, in which one chelate compound ML with stability constant K_{ML} is formed at $a = C_L/C_M > 1$, the concentration of free metal ion in the solution is given by the equation:

$$[M] = \frac{C_M}{1 + (a-1) K_{ML} C_M} . \quad (12)$$

If K_{ML} is sufficiently large, we have

$$[M] = \frac{1}{(a-1) K_{ML}} . \quad (13)$$

For a system consisting of a ligand L with total concentration C_L and an excess of a metal ion N with total concentration C_N, in which one chelate compound NL with stability constant K_{NL} is formed at $b = C_L/C_N > 1$, the concentration of free ligand in the solution is given by the equation:

$$[L] = \frac{1}{(b-1) K_{NL}} . \quad (14)$$

It follows from Eqns. (13) and (14) that in solutions containing a metal ion M and an excess of ligand L ($a = C_L/C_M > 1$) or a ligand L and an excess of a metal ion N ($b = C_N/C_L > 1$), the concentration of the metal ion [M] or [L] respectively depends only on the ratio of the total concentrations of the metal ion (C_M or C_N) and ligand C_L, but is independent of their absolute values, that is, these solutions exhibit buffer properties.

The example involving the buffering of a metal ion M in an excess of a masking ligand L (pM buffer) is of greatest importance in the solution of various problems of masking.

Let us examine the behaviour of a pM buffer in the presence of an ion A which reacts with the metal ion M to form, for example, a sparingly soluble compound MA. In the system we have competition between two reactions: the masking reaction:

$$M + L \rightleftarrows ML$$

and the reaction being masked:

$$M + A \rightleftarrows MA$$

and the effect of the competition is described quantitatively by the equation

$$\lg \frac{[L]}{[ML]} = \lg \frac{1}{K_{ML} K_{sp}} + \lg [A] . \quad (15)$$

It can be seen from Eqn. (15) that the ratio [L]/[ML] should be constant at constant concentration of the excess of precipitant ion [A]. The addition of ML to this system necessarily leads to the dissociation of ML and the precipitation of the liberated M as MA, and the addition of free masking agent L leads to the dissolution of part of the MA precipitate and reaction of the liberated metal ion to form the chelate compound ML until the original value of [L]/[ML] in the solution is restored. The ratio [L]/[ML] in the solution will again control [M] only after the disappearance of the solid phase as a result of the gradual addition of L.

The expression $1/K_{ML}K_{sp}$, in Eqn. (15), called the "precipitation constant" and denoted by K_p, provides a quantitative measure of the tendency for the metal ion to be precipitated from the chelate buffer solution: the greater K_p, the greater the quantity of masking agent required to mask the precipitation. Table 3 gives as an example the values of the precipitation constants for the precipitation of the oxalates of various metals in the presence of various masking agents.

If the masking ligand L is a weak acid, pM also depends on pH; for this example, Eqn. (15) becomes

$$\lg \frac{[L]}{[ML]} = \lg \frac{K_m K_{m-1} \cdots K_2 K_1}{K_{ML} \cdot K_{sp}} + \lg [H_m L] + mp\mathrm{H} , \quad (16)$$

where $K_1, K_2, \ldots, K_{m-1}, K_m$ are the consecutive dissociation constants of H_mL.

Table 2. Logarithmic values of $\alpha_{L(H)}$ for various masking agents*.

pH	TEA	en	den	tren	trien	tetren	penten	EDTA	NTA	DCTA	EGTA	CN^-	F^-	PO_4^{3-}	$P_2O_7^{4-}$	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$HC_6H_4O_7^{3-}$
0	7.8	17.4	23.7	28.7	29.4	34.1	37.9	21.4	14.4	24.1	23.3	9.2	3.05	20.7	18.1	5.1	7.0	13.5
1	6.8	15.4	20.7	25.7	25.4	29.1	33.9	17.4	11.4	20.1	19.3	8.2	2.05	17.7	14.4	3.35	5.0	10.5
2	5.8	13.4	17.7	22.7	21.5	24.1	29.9	13.7	8.7	16.2	15.6	7.2	1.1	15.0	11.3	2.05	3.05	7.5
3	4.8	9.4	14.7	19.7	17.8	19.6	25.9	10.8	7.0	12.8	12.7	6.2	0.3	12.6	8.7	1.05	1.4	4.8
4	3.8	6.2	11.8	16.7	14.1	15.5	21.9	8.6	5.8	10.1	10.5	5.2	0.05	10.6	6.6	0.3	0.4	2.7
5	2.8	5.1	9.3	13.7	11.0	11.9	17.9	6.6	4.8	8.0	8.5	4.2		8.6	4.6	0.05	0.05	1.2
6	1.8	4.1	7.2	10.7	8.1	8.7	13.9	4.8	3.8	6.2	6.5	3.2		6.6	2.9			0.25
7	0.9	3.1	5.2	7.7	5.5	5.7	9.9	3.4	2.8	4.9	4.5	2.2		5.0	1.6			0.05
8	0.2	2.1	3.3	4.8	3.3	3.0	6.0	2.3	1.8	3.8	2.5	1.2		3.7	0.6			
9		1.1	1.5	2.3	1.5	1.0	2.6	1.4	0.9	2.8	0,9	0.4		2.7	0.1			
10		0.4	0.4	0.7	0,3	0.1	0.6	0.5	0.2	1.8	0,1	0.1		1.7				
11		0.1		0.1				0.1		0.9				0.8				
12										0.2				0.2				

* en represents ethylenediamine, den diethylenetriamine, trien triethylenetetramine, tetren tetraethylenepentamine, penten pentaethylenehexamine, TEA triethanolamine, tren triaminotriethylamine, EDTA ethylenediaminetetra-acetic acid, NTA nitrilotriacetic acid, DCTA 1,2-diaminocyclohexanetetra-acetic acid, and EGTA ethylene glycol bis-(2-aminoethyl ether)tetra-acetic acid [presumably 2,2'-ethylenedioxybis(ethyliminodiacetic acid) (Ed. of Translation)].

To calculate the concentration of free metal ion [M] in the pM buffer (that is, in a solution containing the metal ion M and an excess of masking agent L), it is more convenient to use the equation derived in terms of the analytical (total) concentrations of the metal ion C_M and the masking ligand C_L:

$$[M] = \frac{C_M}{1 + K_{ML}(C_L - C_M)}. \quad (17)$$

In the general case, when the masking agent L is a weak acid, it is necessary to use Eqn. (11), which is equivalent

Table 3. Precipitation constants for metal oxalates in the presence of various masking agents [12]*.

M	pK_{sp}	EDTA		NTA		HIDA		DHEG	
		$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p
Cu	7.5	18.3	$1.6\cdot10^{-11}$	12.7	$6.3\cdot10^{-6}$	10	—	8.2	$2.0\cdot10^{-1}$
Pb	10.6	18.2	$1.6\cdot10^{-8}$	11.8	$2.0\cdot10^{-1}$	9.4	13	—	—
Zn	8.8	16.1	$5.0\cdot10^{-8}$	10.4	$2.5\cdot10^{-2}$	8.6	1.6	5.4	2500
Cd	7.8	16.4	$2.5\cdot10^{-9}$	9.8	10^{-2}	7.1	5.0	4.8	1000
Ca	8.7	10.6	$1.3\cdot10^{-2}$	6.4	200	4.8	7900	—	—
Mg	4.1	8.7	$2.5\cdot10^{-3}$	5.4	$2.0\cdot10^{-2}$	3.5	4.0	1.2	795

* EDTA represents ethylenediaminetetra-acetic acid, NTA nitrilotriacetic acid, HIDA *N*-hydroxyethyliminodiacetic acid, and DHEG dihydroxyethylglycine.

to the replacement of the ordinary constant K_{ML} by the conditional constant $K_{ML'}$:

$$[M] = \frac{C_M}{1 + K_{ML'}(C_L - C_M)}. \quad (18)$$

$K_{ML'} = K_{ML}/\alpha_{L(H)}$ and $\alpha_{L(H)} = (C_L - C_M)/[L]$.

If x denotes the fraction of the metal ion M remaining in solution in the presence of the precipitant ion A, Eqn. (18) becomes

$$[M] = \frac{C_M x}{1 + K_{ML'}(C_L - C_M x)}. \quad (19)$$

Making use of the relationship $[M] = K_{sp}/[A]$, we obtain

$$x = \frac{1 + K_{ML'}C_L}{\left(K_{ML'} + \frac{[A]}{K_{sp}}\right)C_M}. \quad (20)$$

Since $K_{ML'}C_L \gg 1$, we obtain finally:

$$x = \frac{C_L}{\left(1 + \frac{[A]}{K_{ML'}K_{sp}}\right)C_M}. \quad (21)$$

For the formation of a metal hydroxide $M(OH)_n$, Eqn. (21) becomes

$$x = \frac{C_L}{\left(1 + \frac{K_w^n}{K_{ML'}K_{sp}[H^+]^n}\right)C_M}. \quad (22)$$

Let us now consider the pL buffer, which is also of importance in the theory of masking by virtue of its use as masking agent (instead of free ligand) in buffer masking.

In the pL buffer, consisting of a masking ligand L and an excess of an indifferent metal ion N ($K_{NL} < K_{ML}$), the concentration [L] is buffered when its value is low (at a low level) and is determined by Eqn. (14).

When the pL buffer is introduced into a solution containing the metal ion M to be masked, the formation of the chelate compound NL in the pL buffer can be regarded, like the formation of the proton complexes H_mL, as a side-reaction with respect to the reaction being masked (between M and L), so that the conditional constant $K_{ML'}$ in Eqn. (18) is given by

$$K_{ML'} = \frac{K_{ML}}{\alpha_{L(H,N)}}, \quad (23)$$

where $\alpha_{L(H,N)} = \alpha_{L(H)} + \alpha_{L(N)}$.

In the presence of the precipitant ion A the value of b in Eqn. (14) depends on the value of x in Eqn. (21)—that is, $b = C_N/(C_L - C_M x)$—so that Eqn. (14) becomes

$$[L] = \frac{1}{K_{NL}\left(\frac{C_N}{C_L - C_M x} - 1\right)}. \quad (24)$$

Eqn. (18) can be used to construct graphs giving the pH dependence of pM, and Eqn. (21) can be used to construct graphs giving the pH dependence of $\lg x$. These graphs, called pM–pH diagrams, provide a convenient means of predicting the efficiency of the masking of various reactions in the presence of free or complexed ligands as masking agents. Fig. 1 gives as an example the pM–pH diagrams for the masking of the formation of $Fe(OH)_3$ in the presence of EDTA, and also in the presence of Ca–EDTA.

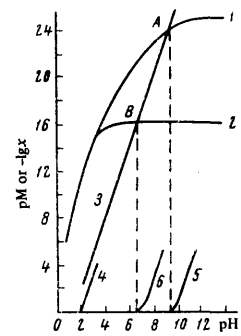


Figure 1. pM–pH and $\lg x$–pH diagrams [10].

Curve *1* gives the pH dependence of pFe in the presence of an excess of EDTA, curve *2* gives the pH dependence of pFe in the presence of a pL buffer consisting of EDTA and an excess of Ca, curve *3* gives the pH dependence of pFe in the absence of masking agent; and curves *4*, *5*, and *6* give the pH dependence of the negative logarithm of the fraction of Fe remaining in solution under the conditions corresponding to curves *1*, *2*, and *3*. The points of intersection of curves *1* and *2* with curve *3* (*A* and *B*) correspond to the start of the precipitation of $Fe(OH)_3$.

4. Other Methods

In addition to the two general methods of calculating the efficiency of masking, described above, various particular methods have been proposed, in which attempts are made to obtain a clearer and simpler description of the equilibrium state in systems containing masking agents and ions being masked, by the introduction of various formally specific masking criteria. Two of these methods deserve mention: Cheng's selectivity ratio method [13], and Hulanicki's masking coefficient method [18].

The first method introduces the concept of "selectivity ratio", defined as

$$\text{S.R.} = \frac{(pM_p)^a}{pM_m}, \qquad (25)$$

where pM_p and pM_m are the negative logarithms of the concentrations of the metal ion resulting from the dissociation of the compound of the metal with the analytical reagent (the product of the reaction being masked) and the complex of the same metal with the masking agent (the product of the masking reaction) respectively.

Calculation of the selectivity ratio, from the pM values determined experimentally or calculated from the thermodynamic or conditional equilibrium constants, makes it possible to predict which of the reactions—the reaction being masked or the masking reaction—predominates in the given system. If the value of the S.R. is less than 7, the masking reaction takes place preferentially in the system (the metal ion is masked), but if the S.R. is greater than 7, masking does not take place and the reaction to be masked takes place normally. Table 4 gives as an example the results of the calculation of the S.R. for the masking action of EDTA on various reactions of the Ag^+ ion.

Table 4. Reactions of the silver ion in the presence of EDTA [13] (concentration of complexes 1 M; pH 10; $K_{Ag\text{-}EDTA} = 2 \times 10^7$; $pM_m = 3.6$).

Reaction	K_{sp} or K_{MA}	pAg^+ (pM_p)	$\frac{(pM_p)^2}{pM_m}$
$2Ag^+ + 2OH^- \rightleftarrows Ag_2O + H_2O$	$2.0 \cdot 10^{-8}$	3.8	4.0
$2Ag^+ + CrO_4^{2-} \rightleftarrows Ag_2CrO_4$	$1.9 \cdot 10^{-12}$	3.6	3.6
$Ag^+ + IO_3^- \rightleftarrows AgIO_3$	$2.0 \cdot 10^{-8}$	3.8	4.0
$Ag^+ + Cl^- \rightleftarrows AgCl$	$1.0 \cdot 10^{-10}$	5.0	7.0
$Ag^+ + Br^- \rightleftarrows AgBr$	$5.0 \cdot 10^{-13}$	6.1	10.3
$Ag^+ + I^- \rightleftarrows AgI$	$8.5 \cdot 10^{-17}$	8.0	17.8
$2Ag^+ + C_2O_4^{2-} \rightleftarrows Ag_2C_2O_4$	$5.0 \cdot 10^{-12}$	3.5	3.4
$Ag^+ + SCN^- \rightleftarrows AgSCN$	$1.0 \cdot 10^{-12}$	6.0	10.0
$2Ag^+ + S^{2-} \rightleftarrows Ag_2S$	$1.0 \cdot 10^{-50}$	16.3	73.8
$Ag^+ + 2S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)^{3-}$	$1.7 \cdot 10^{-13}$	4.6	5.9
$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^-$	$5.6 \cdot 10^{18}$	6.4	11.4

In the second method, use is made of the concept of "masking coefficient", which gives the total concentration of the metal M present in the solution in equilibrium with an equivalent concentration of the analytical reagent, for example, the precipitant ion A for the masking of a precipitation of the type

$$mM + nA \rightleftarrows M_mA_n.$$

For this reaction the masking coefficient is given by

$$pM' = \frac{1}{m+n}\left(pK_{sp} - n \lg \frac{m}{n}\right) - \frac{m}{m+n} \lg \alpha_M - \frac{n}{m+n} \lg \alpha_A, \qquad (26)$$

where pM′ is the negative logarithm of the total concentration of the metal ion M in the solution [M′], pK_{sp} the negative logarithm of the solubility product of M_mA_n, and α_M and α_A the α-coefficients—see Eqns. (6) and (8). Eqn. (26) is derived by expansion of the expression for the conditional constant for the solubility product of M_mA_n.

The value of pM′ calculated from Eqn. (26) can be used to predict which reaction—the masking reaction or the reaction being masked—takes place in a given system under given conditions. Since in the usual analytical procedures the metal ion concentrations lie in the range 10^{-3}–10^{-5} M, complete masking of the reaction takes place when pM′ < 3, and complete demasking takes place when pM′ > 5. As an example let us consider the masking of the formation of $Ag_2C_2O_4$ ($pK_{sp} = 10.46$) in the presence of 0.1 M EDTA at pH 5. We find from Tables 1 and 2 that $\lg \alpha_{Ag(EDTA)} = 0.5$ and $\lg \alpha_{C_2O_4(H)} = 0.05$, so that pM′ = (1/3) − (10.46 − 0.30) − (2/3)(0.5) − (1/3)(0.05) = 3.36, − 0.34 − 0.02 = 3.00, that is, under the given conditions the formation of $Ag_2C_2O_4$ is masked completely.

IV. MASKING AND THE SELECTIVITY OF REACTIONS

To characterise quantitatively the increase in the selectivity of reactions due to masking, let us consider a solution containing one analytical reagent A and two metal ions M_I and M_{II}, which react with A to form products with different stabilities ($K_{M_IA} > K_{M_{II}A}$). By applying the principles of conditional constants [4,5], that is, by assuming that the reaction

$$A + M_{II} \rightleftarrows M_{II}A$$

is a side-reaction with respect to the reaction

$$M_I + A \rightleftarrows M_IA$$

we find that

$$K_{M_IA'} = \frac{K_{M_IA}}{\alpha_{A(M_{II})}} \qquad (27)$$

and

$$\alpha_{A(M_{II})} = \frac{[A] + [M_{II}A]}{[A]} = 1 + [M_{II}]K_{M_{II}A} \simeq K_{M_{II}A}[M_{II}]. \qquad (28)$$

Substituting the value of $\alpha_{A(M_{II})}$ from (28) in (27) and taking logarithms, we obtain

$$\lg K_{M_IA'} = \Delta \lg K + pM_{II}, \qquad (29)$$

where $\Delta \lg K = \lg K_{M_IA} - \lg K_{M_{II}A}$.

When a masking agent L is introduced into this solution, the metal ions M_I and M_{II} react with L in masking reactions, which, in accordance with the method of conditional constants, can be regarded as side-reactions with respect to the corresponding reactions involving the formation of M_IA and $M_{II}A$. Eqn. (29) then becomes

$$\lg K_{M_I'A''} = \Delta \lg K' + pM_{II} \qquad (30)$$

where

$$\Delta \lg K' = \lg K_{M_I'A} - \lg K_{M_{II}'A}.$$

Thus if M_{II} is not to interfere in the analytical reaction of M_I with A in the presence of L (that is, if M_{II} is to be masked quantitatively), the conditional constant $K_{M'_{II}A}$ should be sufficiently small. For example, in the complexometric titration of M_I, which requires that $\lg K_{M'_IA''} > 7$, M_{II} is masked completely when $K_{M'_{II}A}$ becomes so small that

$$\lg K_{M_I'A} - \lg K_{M_{II}'A} + pM_{II} > 7.$$

As an example, Fig. 2 gives graphs showing the conditional constants for the reactions of various metals with EDTA in the presence and absence of tren (2,2′,2″-triaminotriethylamine) as masking agent. It can be seen from Fig. 2, for example, that in the titration of Ca with EDTA in the presence of 0.1 M tren at pH 10, Cu and Ni are masked almost completely, Fe is partly masked, and Mn is not masked at all.

Thus the presence of appropriate quantities of suitable masking agents produces the required difference in the conditional constants of the analytical reaction and the reaction being masked, so that the analysis becomes selective; a given masking agent is effective, however, only under definite conditions, in particular at definite pH values. The behaviour of a masking agent under different conditions can be predicted on the basis of a theoretical examination

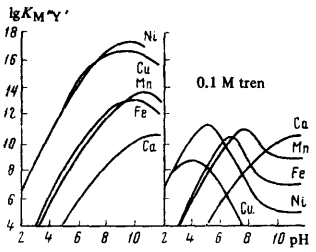


Figure 2. pH dependence of the conditional constants of the complexes of Cu, Ni, Fe, Mn, and Ca with EDTA in the absence and in the presence of an excess of triaminotriethylamine (tren).[5] ($K_{M"Y'} = K_{MY}/\alpha_{M(tren)}\alpha_{Y(H)}$).

of the equilibria established under these conditions. This theoretical approach is greatly facilitated, and the results obtained become extremely clear, if the systems being studied are described by means of diagrams of the type given in Fig. 2 or by means of pA–pH diagrams (pY–pH diagrams for the particular case of complexometry)[7].

V. THE MOST COMMON MASKING AGENTS

A large number of extremely varied inorganic and organic masking agents are now used for the masking of ions and reactions. Table 5 gives common masking agents for the most widely encountered ions of various elements.

Despite the large number and great variety of masking

Table 5. Masking agents for the ions of various elements*.

Element or ion	Masking agent
Ag	CN^-, NH_3, $S_2O_3^{2-}$, SCN^-, TGA, thiourea
Al	F^-, $C_2O_4^{2-}$, CH_3COO^-, OH^-, citrate, tartrate, EDTA, DMP. TEA, Tiron, salicylate, sulphosalicylate, acetylacetonate, malonate, gluconate
As	S_2^{2-}, OH^-, DMP
Au	CN^-, Br^-, $S_2O_3^{2-}$
B	F^-, hydroxy-acids, glycols
Ba	EDTA, citrate, tartrate, NTA, DHEG
Be	F^-, citrate, tartrate, sulphosalicylate
Bi	Citrate, tartrate, EDTA, I^-, Cl^-, NTA, DHEG, thiourea, TEA, DMP, TGA, $Na_5P_3O_{10}$, dithizone
Br	phenols
CN^-	CH_2O, Hg^{2+}, transition metal ions
Ca	EDTA, citrate, tartrate, $P_2O_7^{4-}$, NTA, DHEG
Cd	EDTA, CN^-, $S_2O_3^{2-}$, SCN^-, I^-, citrate, tartrate, NTA, DHEG, DMP, TGA, unithiol, malonate, dithizone
Ce	NTA, EDTA, DHEG, citrate, tartrate, Tiron

Table 5. (con'd).

Element or ion	Masking agent
Cl^-	Hg^{2+}
Co	NH_3, NO_2^-, SCN^-, CN^-, H_2O_2, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate, ethylenediamine, DMP, tren, penten, F^-, $Na_5P_3O_{10}$, malonate, dimethylglyoxime
Cr	EDTA, NTA, DHEG, citrate, tartrate, TEA, ascorbic acid, CH_3COO^-, F^-, NaOH + H_2O_2, $Na_5P_3O_{10}$, Tiron, sulphosalicylate
Cu	NH_3, I^-, SCN^-, CN^-, $S_2O_3^{2-}$, thiourea, EDTA, NTA, DHEG, S^{2-}, DMP, TGA, citrate, tartrate, TEA, tren, penten, NaH_2PO_2, NO_2^-, cysteine
F^-	H_3BO_3, Al^{3+}, Be^{2+}, Fe^{3+}, Zr^{4+}, Ti^{4+}, Th^{4+}, Nb, Ta
Fe	F^-, PO_4^{3-}, $P_2O_7^{4-}$, NTA, EDTA, DHEG, citrate, tartrate, DMP, SCN^-, $S_2O_3^{2-}$, $C_2O_4^{2-}$, CN^-, Tiron, ascorbic acid, thiourea, 1,10-phenanthroline, TGA, TEA, malonate, gluconate, sulphosalicylate, $NH_2OH.HCl$, 2,2′-bipyridyl
Ge	$C_2O_4^{2-}$, F^-
Hf	F^-, H_2O_2, SO_4^{2-}, DHEG, citrate, tartrate, NTA, EDTA, TEA, $P_2O_7^{4-}$, PO_4^{3-}, $C_2O_4^{2-}$
Hg	I^-, SO_3^{2-}, CN^-, NTA, EDTA, DHEG, DMP, Cl^-, citrate, tartrate, TEA, tren, penten, unithiol, thiosemicarbazide, cysteine, TGA
In	TGA
Ir	SCN^-, citrate, tartrate, thiourea
I	Hg^{2+}
Mg	NTA, DHEG, EDTA, $C_2O_4^{2-}$, citrate, tartrate. $P_2O_7^{4-}$, F^-, glycols, TEA
Mn	F^-, $C_2O_4^{2-}$, $P_2O_7^{4-}$, NTA, EDTA, DHEG, citrate, tartrate, DMP, TEA, CN^-, Tiron, sulphosalicylate, oxidising agents
Mo	SCN^-, $C_2O_4^{2-}$, F^-, H_2O_2, citrate, tartrate, EDTA, NTA, DHEG, Tiron, ascorbic acid, $Na_5P_3O_{10}$, $NH_2OH.HCl$
NH_4^+	CH_2O
Nb	F^-, OH^-, citrate, tartrate, $C_2O_4^{2-}$, H_2O_2, Tiron
Ni	CN^-, SCN^-, NTA, EDTA, DHEG, NH_3, citrate, tartrate, tren, F^-, penten, malonate, sulphosalicylate, $Na_5P_3O_{10}$
NO_2^-	sulphanilic acid
Os	CN^-, SCN^-, thiourea
Pb	I^-, CH_3COO^-, $S_2O_3^{2-}$, citrate, tartrate, NTA, EDTA, DHEG, SO_4^{2-}, unithiol, DMP, TGA, $Na_5P_3O_{10}$
Pd	CN^-, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate, TEA, acetylacetone
Pt	NH_3, I^-, CN^-, NO_2^-, SCN^-, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate
Rh	thiourea, citrate, tartrate
Ru	thiourea
S	CN^-, S^{2-}, SO_3^{2-}
S^{2-}	S
SO_3^{2-}	Hg^{2+}, CH_2O
Sb	citrate, tartrate, DMP, I^-, S^{2-}, OH^-, F^-, S_2^{2-}, $S_2O_3^{2-}$, EDTA
Sc	tartrate
Se	S^{2-}, SO_3^{2-}, tartrate, citrate, I^-, F^-, reducing agents
Sn	citrate, tartrate, DMP, F^-, I^-, $C_2O_4^{2-}$, OH^-, TEA, TGA, PO_4^{3-}
Sr	NTA, EDTA, DHEG, citrate, tartrate
Ta	F^-, OH^-, citrate, tartrate, H_2O_2
Te	I^-, F^-, tartrate, citrate, S^{2-}, SO_3^{2-}, reducing agents
Th	F^-, NTA, EDTA, DHEG, citrate, tartrate, TEA, CH_3COO^-, SO_4^{2-}
Ti	SO_4^{2-}, OH^-, H_2O_2, F^-, NTA, EDTA, DHEG, citrate, tartrate, Tiron, TEA, gluconate, sulphosalicylate, ascorbic acid, $Na_5P_3O_{10}$
Tl	Cl^-, CN^-, NTA, EDTA, DHEG, citrate, tartrate, TEA, TGA, $NH_2OH.HCl$
U	F^-, CO_3^{2-}, $C_2O_4^{2-}$, H_2O_2, citrate, tartrate
V	CN^-, H_2O_2, F^-, EDTA, tiron, TEA, ascorbic acid, $NH_2OH.HCl$
W	Tiron, F^-, SCN^-, H_2O_2, tartrate, $Na_5P_3O_{10}$, $NH_2OH.HCl$
Zn	CN^-, NTA, EDTA, DHEG, citrate, tartrate, SCN^-, DMP, OH^-, NH_3, glycols, tren, penten, unithiol, TGA, F^-, $Na_5P_3O_{10}$, dithizone
Zr	F^-, SO_4^{2-}, citrate, tartrate, NTA, EDTA, DHEG, H_2O_2, $P_2O_7^{4-}$, PO_4^{3-}, $C_2O_4^{2-}$, TEA

* DMP represents dimercaptopropanol, and TGA thioglycollic acid; see Tables 2 and 3 for the other abbreviations.

agents, they can be grouped into several classes, of which the most important are the aminopolycarboxylic acids, the polyamines, the hydroxy-acids, and the polyphosphates.

The aminopolycarboxylic acids (complexones)[8,9,12-16,19-30] have molecules containing chelating amino- and carboxyl groups, and form stable water-soluble chelate compounds with a large number of metal ions, including the ions of the alkali and alkaline earth metals. They have a number of advantages over other chelating reagents as masking agents: (1) the high efficiency of masking, due to the high stability of the metal-chelates formed by the complexones; (2) the universal nature of the masking, resulting from the ability of the complexones to form comparatively stable chelate compounds with almost all known metals; (3) the wide pH range of masking, related to the high stability of the metal-chelates formed by the complexones and the comparatively low stability of their proton complexes; (4) the possibility of masking at relatively high temperatures, due to the thermal stability of the complexones and their metal-chelates in aqueous solutions; (5) the compatability of the complexones with the other components of usual analytical systems, related to their ability to function in many other capacities (as titrants, pH regulators, photometric reagents, etc.).

The complexone with the most useful properties and widest application is ethylenediaminetetra-acetic acid (EDTA). It reacts with metal ions usually as a sexidentate ligand by coordination through the two nitrogen atoms of the two amino-groups and four oxygen atoms of the four carboxyl groups. The resulting chelates have an octahedral structure with little steric distortion, stabilised by the presence of several five-membered rings and showing a stereochemistry favourable for most common metal ions. In EDTA the common tendency of the carboxyl group to form complexes is strengthened by the chelating effect, resulting in an increase in the stability of the chelate compounds compared with the corresponding complexes formed from the unidentate complexes without ring closure. As a result, EDTA exhibits chelating properties with respect to the ions of almost all metals; this makes it a universal masking agent, but it is not specific.

The selectivity of the masking action of EDTA can be increased slightly, however, by controlling the pH of the solutions. Masking by EDTA is most effective in weakly acidic and alkaline solutions.

Under optimal conditions of acidity, EDTA reacts with most metal ions to form complexes with a cation: ligand molar ratio of 1 : 1. Protonated complexes may be formed in strongly acidic solutions, and mixed hydroxo-complexes may be formed in strongly alkaline solutions. The formation of chelate compounds with molar ratio 1 : 2 is observed only for quadrivalent metals.

Attempts to modify the structure of EDTA in order to improve its coordinating properties have not in general given satisfactory results. Exhaustive data on the results of these studies, which are of undoubted theoretical importance, are given in a review by Dyatlova and Lastovskii[30], so that we shall mention only a few features which are of interest for increasing the efficiency and selectivity of masking. The closure of the alicyclic ring in *trans*-1,2-diaminocyclohexanetetra-acetic acid (DCTA), accompanied by a decrease in the freedom of rotation of the amino-groups in the ligand and the formation of an additional ring in the structure, leads to a marked increase in the stability of the chelate compounds formed with all metals and to a decrease in the rate of chelation; replacement of the cyclohexane ring by cyclopentane or cycloheptane rings gives complexones whose stabilities are respectively greater or less than the stability of DCTA, but greater than the stability of EDTA. Increase in the denticity of the ligand by the introduction of additional iminoacetate groups into the EDTA molecule (diethylenetriaminepenta-acetic, triethylenetetraminehexa-acetic, and tetraethylenepentaminehepta-acetic acids) brings about a selective increase in the stability of the chelate compounds for highly-charged metal ions. Replacement of the hydrogen atoms attached to the carbon atoms of the methylene groups by methyl groups (1,2-diaminopropanetetra-acetic and 2,3-diaminobutanetetra-acetic acids) leads to greater solubility of the complexones and to higher stability in the chelate compounds of various metals. The tetra-acetic acids of amino-ethers (ethyl etherdiaminetetra-acetic and glycol etherdiaminetetra-acetic acids†) combine more readily with the ions of the heavy alkaline earth metals (Ca^{2+}, Sr^{2+}, and Ba^{2+}) than with magnesium ions.

To conclude the list, it can be stated in general that special reconstruction of the complexone molecule by the introduction of hetero-atoms and functional groups, by changing the distance between the iminodiacetate groups or between the nitrogen and the carboxyl group, by replacing the methylcarboxyl groups by hydroxyethyl and methylphosphinic groups, by increasing the rigidity of the entire system, and by breaking down the electron density of individual units, produces chiefly selective reagents, but does not always lead to an increase in the stability of the complexes formed.

Of the known complexones, the most important masking agents are EDTA, DCTA, and nitrilotriacetic acid. These are widely used in qualitative analysis[19-22,25,30], gravimetric analysis[4,5,8,9,12,13,15,19,20,22,26-29], complexometric titration[4-9,12-15,19,20,22-30], photometry[4,5,8,9,15,19,20,22,27-30], polarography[8,9,12,15,19,20,22,27-30], ion-exchange chromatography[12,15,19,20,22,27-30], and a number of other analytical procedures.

Polyamines[12-14], like aminopolycarboxylic acids, contain several donor nitrogen atoms and are multidentate ligands. Thus complex formation with these compounds also involves simple stoichiometry (the chelate compounds formed with metal ions usually have cation: ligand molar ratio equal to 1 : 1) and a chelating effect (leading to the production of chelate compounds with five- or six-membered rings, which are more stable than the complexes with simple ammonia molecules).

The selectivity of polyamines in complex formation with metal ions is greater than that of the complexones, since the strength of the ligand field for amine ligands is greater than that for carboxylic acid ligands. With metal ions which react more readily with donor nitrogen than with oxygen (Cu, Ni, Co, Zn, Cd, and Hg), they form water-soluble chelate compounds with stability constants which differ fairly sharply (Table 6), whereas they undergo almost no reaction with alkaline earth metal ions.

The data in Table 6 first of all illustrate the chelating effect, that is, the effect of combining the donor groups into a single common molecule. For example, comparison of $\lg\beta_1$(Cu-En) (10.55) with $\lg\beta_2$ (Cu-2NH_3) (7.61) shows that the formation of one five-membered chelate ring in the ethylenediamine complex of copper increases the stability of the latter by a factor of ~ 1000 relative to the stability of the copper ammine formed by the coordination of

† Possibly 2,2′-oxybis(ethyliminodiacetic acid) and ethylenedioxybis-(methyliminodiacetic acid) are intended (Ed. of Translation).

Table 6. Stability constants of complexes of metals with amines (temperature 20°C, ionic strength $I = 0.1$).

Ion	NH_3				en			dien		trien	tetren	penten	tren	EDTA
	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_1$	$\lg\beta$	$\lg\beta_1$
Ag^+	3.40	7.40	—	—	4.7	4.7	—	6.01	—	7.7	—	—	7.8	7.3
Cd^{2+}	2.60	4.65	6.04	6.92	5.47	10.02	12.09	8.45	13.85	10.75	14.0	16.8	12.3	16.5
Co^{2+}	2.05	3.62	4.61	5.31	5.89	10.72	13.82	8.1	14.1	11.0	15.1	15.75	12.8	16.3
Cu^{2+}	4.13	7.61	10.48	12.59	10.55	19.60	—	16.0	21.3	20.4	24.3	22.44	18.8	18.8
Fe^{2+}	1.4	2.2	—	3.7	4.28	7.53	9.52	6.23	10.36	7.8	11.4	11.20	8.8	14.3
Hg^{2+}	8.80	17.50	18.5	19.4	—	23.42	—	21.8	25.06	25.26	27.7	29.59	22.8	21.8
Mn^{2+}	0.8	1.3	—	—	2.73	4.79	5.67	3.99	6.82	4.9	7.62	9.37	5.8	14.0
Ni^{2+}	2.75	4.95	6.64	7.79	7.66	14.06	18.59	10.7	18.9	14.0	17.6	19.30	14.8	18.6
Zn^{2+}	2.27	4.61	7.01	9.06	5.71	10.37	12.08	8.9	14.5	12.1	15.4	16.24	14.65	16 5

two unidentate NH_3 ligands to Cu^{2+}. Table 6 also shows that the increase in the number of chelating rings in the 1 : 1 complexes for a given metal on going from ethylenediamine to penten (that is, with increase in the multidenticity of the ligand) leads to a progressive increase in the stability constants of the chelate compounds and to a gradual decrease in the tendency for the metal ion to combine with a second molecule of the ligand.

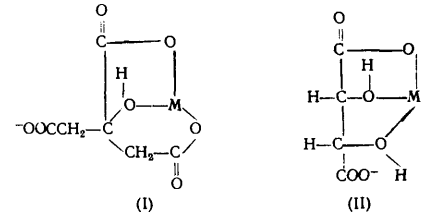
Of the above polyamines, tren, trien, tetren, and penten are most widely used as masking agents. A disadvantage of the polyamines as masking agents is their extreme sensitivity to inorganic acids, resulting from their ability to combine with several protons. Moreover, commercial polyamine specimens are always contaminated with lower amines and are difficult to purify, and this hinders their study and practical application.

Hydroxy-acids[12,13,31] have molecules containing chelating hydroxyl and carboxyl groups and act as multidentate ligands which are much weaker than the nitrogen-containing multidentate ligands (aminopolycarboxylic acids and polyamines). Moreover, they have a greater tendency, compared with the polyamines, to react with metal ions by a stepwise mechanism with the formation of chelate compounds with cation : ligand molar ratios of 1 : 1, 1 : 2, etc.; mixed complexes and polynuclear complexes may also be formed.

Table 7. The stability constants of the tartrato- and citrato-complexes of various metals in acid medium (1 : 1 type) (temperature 20°C, ionic strength $I = 0.5$).

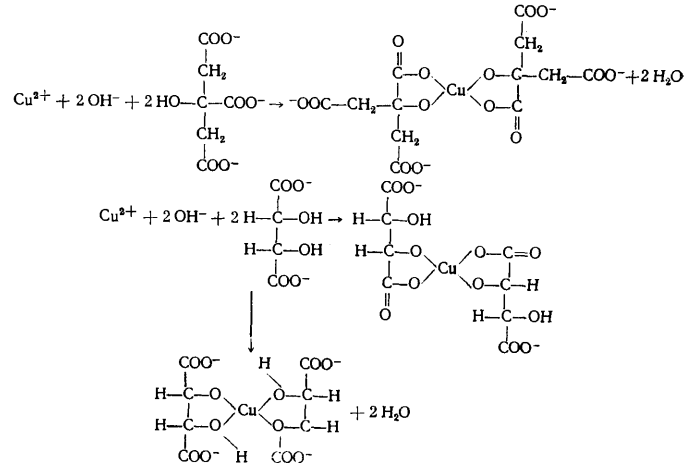
Ligand	lgβ								
	Ba	Ca	Cd	Co	Cu	Mg	Pb	Sr	Zn
Tartrate $(CHOHCOO)_2^{2-}$	1.5	1.7	2.8	2.1	3.2	1.2	3.8	1.4	2,4
Citrate $C_4H_4OH\,(COO)_3^{3-}$	2.4	3.5	4.0	4.4	6.1	2.8	5.2	2.8	4.5

The properties and stabilities of the chelate compounds formed depend on the number and mutual arrangement of the carboxyl and hydroxyl groups in the hydroxy-acid molecule, and also on the ability of these groups to give up hydrogen ions; this in turn is related to the pH of the solution. Comparison of the stabilities of the citrato- and tartrato-chelates of various metals formed in acid medium (Table 7) shows that the citrato-chelates are more stable than the tartrato-compounds. This is due to the fact that the coordination of the citrate ion to the metal ion leads to the formation of two stable rings including two strongly bonding carboxyl groups and one hydroxyl group (I), whereas the coordination of the tartrate ion is accompanied by the formation of two rings containing two weakly bonding hydroxyl groups and one carboxyl group (II); moreoever, the stabilities of these chelate compounds are also influenced by the magnitude of the charge on the ion (−3 for citrate and −2 for tartrate).



(I) (II)

Because of the comparatively low stability of their chelate compounds, the hydroxy-acids have a low efficiency as masking agents in acid medium, particularly for alkaline earth metal ions. Their masking power increases considerably, however, in alkaline medium (at pH > 10), in which they react with metal ions to form extremely stable chelate compounds, probably with the participation of alkoxy-groups:



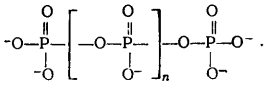
The formation of chelate compounds containing alkoxy-bonds may take place not only in strongly alkaline solutions, in which optimal conditions are created for the formation of alkoxide ions, but also in acidic solutions, if the

metal ion has a sufficiently high polarising power. For example, the Fe^{3+} ion brings about "induced dissociation" of the hydroxyl proton of the hydroxy-acid and forms stable chelate compounds with hydroxy-acids even in acidic solutions.

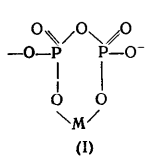
The participation of alkoxide groups in chelate formation probably explains the fact that in alkaline solutions the tartrato-complexes are more stable than the citrato-complexes. It is also of interest to relate the increased stability of the complexes formed by hydroxy-acids in alkaline solutions with the possibility of formation, under these conditions, of mixed dinuclear complexes containing both hydroxide ions and hydroxy-acid anions as ligands[27].

The hydroxy-acids most frequently used as masking agents are tartaric and citric acids, mentioned above, and also malonic, gluconic, and salicylic acids. Tartaric and citric acids are in most instances interchangeable, but there are instances in which the use of one or the other is to be preferred, apparently due to differences in the stabilities of their chelate compounds at different pH values.

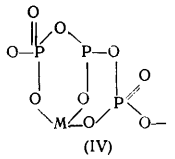
Polyphosphates[12,33], which are used as masking agents, are inorganic linear polymers whose chain structure contains four oxygen atoms arranged tetrahedrally around each phosphorus atom



They react with many metal ions, particularly the alkaline earth metal ions, to form water-soluble polymeric complexes with a six-membered chelate structure, in which the metal ion is joined to two or more negatively charged oxygen atoms attached to neighbouring phosphorus atoms (I–III):



(I)



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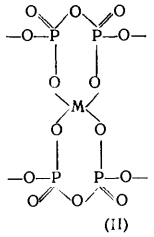
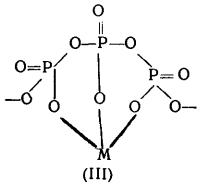


(II)



(III)

Because of the complexity of the structures of the polyphosphates, it is difficult to characterise quantitatively their reactions with metal ions. The published formation constants for the chelates of various polyphosphates (Table 8) indicate, however, that the stabilities of their chelates increase with increase in the length of the polyphosphate chain (that is, with increase in the multidenticity of the ligands).

A serious disadvantage of the polyphosphates as masking agents is their tendency to undergo hydrolysis with the formation of orthophosphate ion, which is able in turn to precipitate the ions of many metals. The rate of hydrolysis depends on many factors (pH, temperature, degree of dehydration of the polyphosphate, etc.), including the length of the polyphosphate chain (the degree of hydrolysis increases rapidly with increase in chain length). The hydrolysis of polyphosphates is catalysed by hydrogen ions, and also by the ions of various metals, the catalytic effect of the latter being directly proportional to their Lewis acid strength ($Cu^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+}$).

Table 8. Formation constants of chelates for various polyphosphates (temperature 20°C, ionic strength $I = 0.1$).[12]

Polyphosphate	Chain length n	lgβ		
		BaL	CaL	MgL
Sodium pyrophosphate $Na_4P_2O_7$	2	4.5	–	–
Sodium tripolyphosphate $Na_5P_3O_{10}$	3	4.5	–	–
Sodium tetrapolyphosphate $Na_6P_4O_{13}$	4	5.5	–	–
Vitreous sodium polyphosphate	7.5	6.0	–	–
Vitreous sodium polyphosphate	8.5	6.5	–	–
Adenosine monophosphate	0	–	1.41	1.69
Adenosine diphosphate	1	–	2.78	3.11
Adenosine triphosphate	2	–	3.60	4.00

The masking action of polyphosphates with respect to alkaline earth metal ions is widely used in technology for water softening. Organic polyphosphates are of considerable interest in biology; in particular, adenosine triphosphate apparently acts as a universal accumulator and distributor of the chemical energy of nutrients and as the chief energy donor in all fundamental reactions of biosynthesis in the organism, and also in such important physiological processes as muscle contraction and higher nervous activity.

In analysis, the polyphosphates most widely used for masking are sodium pyrophosphate $Na_4P_2O_7$, sodium triphosphate $Na_5P_3O_{10}$, and sodium hexaphosphate $Na_6P_6O_{18}$. Sodium triphosphate in neutral and alkaline media forms water-soluble complexes with the ions of a large number of metals, including Li, Be, Mg, Ca, Sr, Ba, Zn, Cd, Fe^{II}, Fe^{III}, Co, Ni, Mn, Cu, Pb, V, Al, Y, In, La, Ce^{III}, Pr, Nd, Ag, Hg^{I}, Ti, Zr, Bi, Sn^{II}, Sn^{IV}, Th, and U^{VI}.

The following compounds are not precipitated in the presence of $Na_5P_3O_{10}$: the hydroxides, phosphates, carbonates, and borates of all the above elements; calcium fluoride, oxalate, tartrate, and citrate; and lead fluoride, chromate, and sulphate; similarly, iron(III) sulphosalicylate and sulphide are not formed. $Na_5P_3O_{10}$ does not prevent the precipitation of zinc, mercury, lead, and copper sulphides, however.

Of the other known masking agents, extensive use in chemical analysis is made of cyanide, fluoride, and triethanolamine[13]. Cyanide is a very effective masking agent for the elements of Groups IB, IIB, and VIII of the Periodic Table, since extremely stable soluble complexes are formed; cyanide is used chiefly in alkaline or neutral solutions—its use in acid solutions is undesirable because of the formation of toxic hydrogen cyanide. Fluoride forms stable soluble complexes with Be, Al, Fe, Si, Ge, B, Sm, Sb, Ti, Zr, Hf, the rare-earth elements, etc., and is often used to mask these elements. Triethanolamine (2,2,2-nitrilotriethanol) is an effective masking agent for Al, Fe, Mn, and various other highly-charged ions; it prevents the hydrolysis of tervalent and quadrivalent metals at high pH.

VI. CHARACTERISTIC EXAMPLES OF THE PRACTICAL APPLICATION OF MASKING

Any type of chemical reaction—precipitation, oxidation–reduction, complex formation, etc.—can be subjected to masking under various circumstances. Thus masking may be used in all chemical and physicochemical methods of analysis in which a chemical reaction takes part in any form. It can confidently be stated that most papers now published on chemical analysis deal to some extent with the masking of reactions and ions; in a number of instances masking is an essential step in the analytical methods or procedures recommended or described in these papers. It is therefore understandable that a short review cannot give exhaustive data on the practical application of the masking of reactions and ions in chemical analysis. In the present review, therefore, we shall merely refer to published reviews on the use of masking in qualitative analysis [2,3,20-22,25], gravimetric analysis [3,8,9,12,13,20,22,26], complexometric titration [14,20,22,23,27,28], photometry [3,8,9,20,22], polarography [8,9,12,15], and ion-exchange chromatography [12,15,20], and examine some characteristic examples of application of masking.

In most instances the masking of the reaction of a given ion is required when it is necessary to eliminate the interfering influence of this ion when carrying out the analogous reaction of another ion with the same reagent. In equilibrium masking this is achieved by decreasing the concentration of the interfering ion or reagent, and in most instances the mechanism of masking is based on the formation of soluble complexes of the interfering ion or reagent with the masking agent. The necessary decrease in the concentration of the interfering ion naturally depends on the method of analysis employed; in spectrophotometry, for example, the concentration of the interfering ion should be very low, whereas in complexometric titration the conditions of masking are much less severe.

The masked form of the interfering ion must often satisfy additional special requirements in addition to the main requirement of stability, ensuring the necessary decrease in the concentration of the interfering ion. The nature of these additional requirements depends on the analytical method: in gravimetric analysis the masked form should not be coprecipitated with the analytical form, in spectrophotometry the masked and analytical forms should absorb light in different ranges of the spectrum, in redox titrations they should have different redox potentials, in ion exchange they should have different affinities for the ion exchanger, etc.

The satisfactory fulfillment of the main and additional requirements by the masked forms of various ions creates the prerequisite for another widely encountered example of the use of masking, namely for the determination of these ions when present together, or for their separation. The efficiency of the simultaneous determination and separation of ions using masking is particularly high when the abilities of these ions to be masked by given masking agents and to take part in analytical reactions with a given reagent change in the opposite sense.

A large number of examples of the use of masking to eliminate the interfering influence of accompanying ions, to determine various ions when present together, and to separate these ions, that is, examples of the use of masking to increase the selectivity of analysis, are given in the reviews cited above; we shall give only two examples as illustration: (1) the increase in the selectivity of the polarographic analysis of the ions of various metals in the presence of DCTA (Table 9) [34], and (2) the increase in the selectivity of the colour reaction of rare-earth metal ions with Methylthymol Blue in the presence of EDTA (Table 10) [35].

The masking of reactions is often used for the direct detection and determination of ions. In addition to the familiar use of the masking of the formation of the zirconium–Alizarin lake in the presence of F^- for the detection and photometric determination of F^-, mention may also be made of the photometric determination of Te from the decrease in the light absorption of a solution of molybdosilicic acid as a result of the partial masking of the formation of the molybdosilicate in the presence of Te^{4+}. [36]

Table 9. Values of $E_{1/2}$ for metal ions in the presence and absence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA).

Metal ion	pH 2.7, 0.4 M CH_3COOH		pH 4.6, 0.4 M CH_3COOH + 0.4 M CH_3COONa		pH 9.5, 0.1 M NH_4OH + 0.1 M NH_4Cl	
	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)
Cu^{2+}	+0.02	−0.16	−0.02	−0.40	−0.29	−0.62
Pb^{2+}	−0.38	−0.85	−0.43	i.a.	—	i.a.
Cd^{2+}	−0.60	−1.04	−0.61	i.a.	—	i.a.
Zn^{2+}	−1.01	i.a.*	−1.03	i.a.	−1.14	i.a.
Bi^{3+}	0.00	−0.47	−0.14	−0.66	—	−0.70
Fe^{3+}	—	−0.11	—	−0.11	—	−0.11
Sn^{2+}	−0.02	−0.14	−0.17	−0.17	—	—
Tl^{1+}	−0.42	−0.42	−0.42	−0.42	0.42	−0.16

* i.a. indicates chelate polarographically inactive.

Table 10. Colours of complexes formed by r.e.e.-EDTA with Methylthymol Blue.

Element	$lg\beta$	4 M NH_3 solution
Y	18.09	pale blue
La	15.50	intense blue
Ce	15.98	ditto
Pr	16.40	»
Nd	16.61	»
Sm	17.14	»
Eu	17.35	»
Gd	17.37	pale blue
Tb	17.93	ditto
Dy	18.30	»
Ho	18.74	none
Er	18.85	»
Tu	19.32	»
Yb	19.51	»
Lu	19.83	pale pink

Mention may also be made of the mechanism of the masking action of masking agents, in particular F^-. The decolorisation of the zirconium–Alizarin lake in the presence of F^- is usually attributed to the formation of colourless ZrF_6^{2-}, and an analogous explanation was previously put forward for all other examples of the determination of F^- based on the decolorisation of the coloured chelate compounds formed by metals with various dyes. It was found, however, that in a number of instances, for example in the photometric determination of F^- from the decrease in the light absorption of a Zr–Xylenol Orange mixture, the decrease in the light absorption is due to the formation of a colourless Zr–F–Xylenol Orange ternary complex [37], that is, the determination of F^- in this instance cannot be regarded as indirect. These examples deserve careful attention in the theoretical examination of the masking of reactions.

In some instances the masking of reactions provides a very convenient and simple method for establishing the stoichiometric composition and determining the stability constants of complexes in aqueous solutions. Thus the decrease in the light absorption of a solution of molybdosilicic acid as a result of the partial masking of the formation of molybdosilicate in the presence of various complexing agents (oxalate, tartrate, or tellurite) can be used to determine the compositions and stabilities of the complexes formed by molybdenum with these complexing agents [38].

The possibilities provided by the use of the masking of reactions and ions for various purposes are not exhausted by the above examples—the number of examples could be greatly extended. In conclusion, mention must be made of another promising application of masking—for the production of an "ideal" blank specimen. The usual method of preparing a blank specimen suffers from one major disadvantage: because of the need to exclude some component of the analytical reaction from the blank specimen, the chemical composition of the latter is not completely identical with that of the specimen being analysed. Masking makes it possible to eliminate this disadvantage in the preparation of a blank specimen. If an additional reagent (the masking agent) is introduced into a blank specimen containing the substance being analysed and all the necessary reagents in the same quantities as in the specimen being analysed, the analytical reaction is frozen (masked) from the beginning; the additional reagent is added to the specimen being analysed only after the analytical reaction is complete. Thus the blank specimen finally has a chemical composition which is completely identical with that of the specimen being analysed, and differs only in the absence of the analytical effect being measured, that is, it is an ideal blank specimen. The value of this new method of preparing a blank specimen has been illustrated, for example, in the photometric determination of silicon [39] and phosphorus [40] as their molybdenum heteropolycomplexes.

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The two types of masking examined at the start of the present paper, namely: (1) equilibrium masking due to a change in the thermodynamic conditions of the reaction being masked, and (2) non-equilibrium masking due to a change in the kinetic conditions of the reaction being masked, cover all examples of the masking of reactions known in practice. The opposite is also true, namely, that almost all chemical reactions can be masked by appropriate means: if a given reaction cannot be masked by influencing its thermodynamic conditions, it can be masked through kinetics and catalysis.

These two forms of masking—equilibrium and non-equilibrium—naturally require different approaches to their theoretical examination. The material given above deals chiefly with the problems of equilibrium masking. This is due to the fact that the techniques of equilibrium masking have been used to a much greater extent up to the present, and the associated problems have undergone corresponding development. Even the few observations and examples which have been published, however, indicate the promising possibilities provided by the use of non-equilibrium (kinetic) masking in addition to equilibrium (thermodynamic) masking.

Non-equilibrium masking is a useful supplement to equilibrium masking, since it is applicable to those systems for which equilibrium masking is unsuitable. An important feature of non-equilibrium masking is the possibility of controlling it by means of the temperature factor.

The kinetics of analytical reactions with particular reference to masking have not been specially studied. It is therefore not yet possible to reach any general conclusions. Recently, however, the importance of a detailed study of the kinetics of analytical reactions, particularly reactions involving complex formation, has been pointed out by a number of authors [5,30,41], particularly Reilley [42], who in addition to other problems discusses the kinetics of the formation and dissociation of metal complexonates, and considers that these problems are the most important at the present stage of the study of complexonates.

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Infrared Spectra of Steroids

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CONTENTS

I. Features of the chemical structure of steroids 155
II. Correlation of the infrared spectra of steroids with their structure 156
III. Use of infrared spectroscopy in steroid chemistry 164
1. Sterols 164
2. Unsaturated steroids 165
3. Steroidal ketones 165
4. Epoxysteroids and lactones 165
5. Methyl- and methylene-steroids. Steroidal acetates 165
6. Halogenosteroids 166
7. Nitrogen-containing steroids 166
8. Conversions of steroids 166
9. Some particular structural problems 166

Valuable information about chemical structure obtained in the study of infrared spectra of individual compounds produces a natural increase in the interest of chemists in molecular spectroscopy.

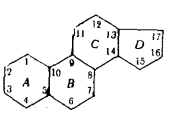
In the Russian literature there are hardly any papers dealing with the infrared spectra of steroids. Furthermore there is not one review on the infrared spectra of the steroids.

This review considers work on the infrared spectra of the steroids during the period from its inception (1939) to 1966.

I. FEATURES OF THE CHEMICAL STRUCTURE OF THE STEROIDS

The main features of the chemical structure of the steroids have now been explained quite definitely. The general principles are reliable, although there are still a greater number of compounds of the steroid series details of whose structure are either unknown or require proof.

The structure of the steroids is based on a complex polycyclic system consisting of three cyclohexane rings and one cyclopentane ring. Such a system is 10,13-dimethylcyclopentanoperhydrophenanthrene, with the accepted numbering of the atoms of the carbon skeleton (I):



(I)

The rings are denoted by the letters A, B, C, and D in accordance with the increasing numbering of the carbon atoms.

There are six asymmetric carbon atoms, so theoretically such a compound can have $2^6 = 64$ stereoisomers but only some of the steroisomeric forms are encountered in natural compounds. From this it follows that the steroid molecules have rigidly fixed spatial conformations, unlike the mobile conformations of cyclohexane.

Sometimes the ring of the steroidal skeleton (ergosterol, 7-dehydrocholesterol, ring B; oestrogen, ring A) contains a C=C double bond. This fixes still more rigidly a definite conformation of the molecule. Despite the non-planar structure of the cyclohexane rings, their combination in a

steroid molecule exhibits a compressed structure—the "thickness" of the plane of the skeleton is ~ 0.8 Å. The cyclohexane rings in the steroidal skeleton have the "chair", not the "boat", conformation.

Free five-membered rings have a non-planar structure thanks to the presence of "Pitzer strain"[1-3]. Clearly, the five-membered ring D in the steroid molecules also has a non-planar conformation, as is shown by certain stereospecific reactions which take place with participation of the functional groups of ring D.

In the sterols and most other steroids side chains of various dimensions are attached to $C_{(17)}$ of the cyclic skeleton.

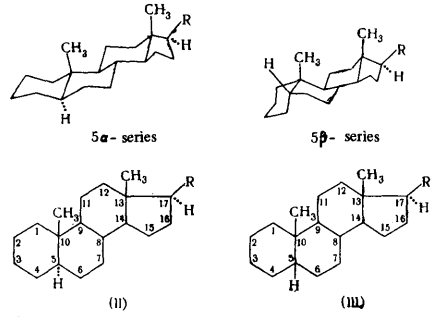
The naming of the steroids depends on the conformation of the cyclic skeleton and the length of the side chain at $C_{(17)}$.

In 1957 the Commission on [the Nomenclature of Organic Chemistry and] the Nomenclature of Biological Chemistry [of the International Union of Pure and Applied Chemistry] issued Definitive Rules for Nomenclature of Steroids.

The conformations of the steroids are distinguished by the type of junction of rings A/B because in all the steroids without exception and their synthetic analogues ring junctions B/C and C/D are the same and are *trans*-fused. Hence there are two steric series of steroids: a series with *trans*-fusion of rings A and B, and a series with *cis*-fusion of rings A and B.

Substituents above the plane of the cyclic system are denoted by the letter β, those beneath the plane by α.

It is easy to see that in the *trans*-fusion of rings A and B the hydrogen atom at $C_{(5)}$ is beneath the plane of the cyclic system, that is, in the α-position (II). With *cis*-fusion at A/B the hydrogen atom at $C_{(5)}$ is in the β-position (III). Therefore the series with A/B *trans*-fusion is termed the 5α-series, and that with A/B *cis*-fusion, the 5β-series.



It has now been shown that in all steroids the side chain at $C_{(17)}$ is in the β position. Unfortunately, investigators working in the field of steroid chemistry have not adhered to unique names for these compounds. Detailed information about the nomenclature of the steroids is given in the Fiesers' monograph[5] and Protiva's paper[6].

A review of the accepted nomenclature of the steroids taking account of the geometrical and optical isomerism has also been given in a special article by Götzky[7] devoted to this question.

II. CORRELATION OF THE INFRARED SPECTRA OF STEROIDS WITH THEIR STRUCTURE

a. C–O Bonds

The C–OH stretching vibrations appear in the infrared spectra of alcohols as an intense band in the 1000–1200 cm^{-1} range. Differences in the position of this band for primary, secondary, and tertiary alcohols were observed by Weniger[8] as long ago as 1910. These researches were continued much later by Tout and Lecomte[9], who also observed a relation between the position of the C–OH band and the structure of the molecule. The more detailed investigations of Zeiss and Tsusui[10] showed the influence of electronic effects and the symmetry of the molecule on the position of this band.

Regular investigations of the infrared spectra of the steroids and particularly the sterols, began about 1946. In one of the first works on the assignment of the bands in the infrared spectra of the sterols, Furchgott and coworkers[11] noted a series of features of the band of the C–OH stretching vibrations. In particular, they showed that the absorption band of the C–O stretching vibrations for the $\rangle$C–OH group is at ~ 1250 cm^{-1}, but when the carbon atom is connected to only single bonds, the absorption takes place in the 1000–1100 cm^{-1} region. They also reported the important fact of the dependence of the position of the C–O band on the mutual arrangement of the substituents at the third and fifth carbon atoms of the steroid skeleton. Thus the 3β-*trans*-5α- and 3α-*trans*-5β-steroids exhibit a band in the 1047–1058 cm^{-1} region, but the 3α-*cis*-5α-steroids have a weaker band with a maximum at 1064 cm^{-1}. Nevertheless a molecule with two OH groups can show only a single C–O bond absorption band (androstan-3β,17α-diol). The same correlation was found by these authors in a subsequent study[12], where they investigated the infrared spectra of the steroids of the pregnane series. Substances of the pregnane series with the 3β-*trans*-5α-configuration are characterised by a band between 1047 and 1058 cm^{-1}. A hydroxyl in the 3β-position and a Δ^5-double bond always produce a band in the 1058–1064 cm^{-1} range and a $C_{(20)}$ hydroxyl, a band at 1079 cm^{-1}. In another paper by the same authors it was noted that a hydroxyl group at $C_{(21)}$ causes an intense band for the C–OH bond between 1073 and 1078 cm^{-1}. Somewhat later (1952) a coauthor of Furchgott's first three papers (Rosenkrantz) and Zabloy[14] made a more detailed examination of the infrared spectra of the steroidal $C_{(3)}/C_{(5)}$ epimers. These investigations refined the results of the first studies. Moreover the range of compounds investigated was extended. Fig. 1 gives their results for the $C_{(3)}/C_{(5)}$ epimers of androstane. Rosenkrantz and coworkers[15] obtained similar results for cholestane, cholest-2-ene, cholest-4-en-3-one, 7-ketocholesterol, and various other compounds. The corresponding infrared frequencies found by the authors[14,15] for various stereoisomeric forms are:

Coprostanol (3β, 5β)	1041 cm^{-1},
Epicoprostanol (3α, 5β)	1062 and 1040 cm^{-1},
Cholestanol (3β, 5α)	1075 and 1041 cm^{-1},
Epicholestanol (3α, 5α)	1038 and 1004 cm^{-1}.

In another study, Rosenknrantz and coworkers[16] investigated the absorption of C–OH bonds in some unsaturated sterols. They assigned the 1053 cm^{-1} band of Vitamin D_2 to the C–OH stretching vibrations and it is evidently characteristic for the opened ring B. However, this correlation cannot be considered to be completely reliable, since in this range of the Vitamin D_2 spectrum there are other bands which are no less intense[17].

At about the same time, two papers by Cole[18] and Cole and coworkers[19] appeared, the latter deserving special attention. It gave proof of the conformational sensitivity of the band of the C–OH stretching vibrations, illustrated by a rather large number of examples. The authors[19] measured the spectra of 72 different steroids and showed conclusively that the band of the C–OH stretching vibrations

is most intense in the 1000–1100 cm^{-1} range and its position is determined by the conformation of the steroid molecule. Table 1 gives the results of Cole and coworkers[19] which charaterise the dependence of the absorption in the 1000–1100 cm^{-1} range on the structural type of the molecule.

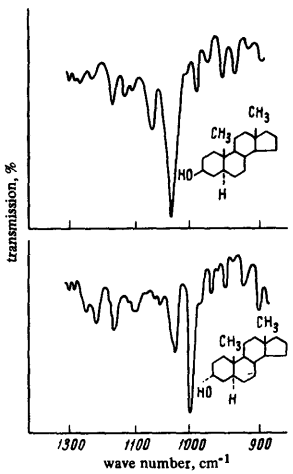


Figure 1. Infrared spectra of $C_{(3)}/C_{(5)}$-epimers of androstane in the 900–1200 cm^{-1} range (see Rosenkrantz and Zabloy[14]).

Table 1. Frequencies of the C–OH stretching vibrations at various orientations of the OH group at $C_{(3)}$ and of the hydrogen atom at $C_{(5)}$ in sterol molecules[19].

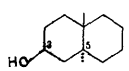
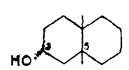
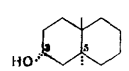
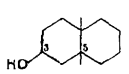
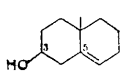
Structural type	Absorption of the most intense band in the 1000–1100 cm^{-1} range	Number of examples
	1037—1040	18
	1036—1040	25
	996—1002	9
	1032—1036	6
	1050—1056	14

Fig. 2 gives the spectra of androstan-3β-ol and coprostan-3α-ol. Both compounds have a *trans*-position for the hydroxyl groups and a hydrogen atom at $C_{(5)}$. As Fig. 2 shows, the side-chain at $C_{(17)}$ has no effect on the position of the maximum of the absorption band for the C–OH stretching vibrations (1039 cm^{-1}). In the same paper they showed[19] that the frequency of this band in hydroxy-steroids also depends on the configuration of the C–O bond itself, and not only on the α- or β-positions of the OH groups relative to the plane of the cyclic part of the molecule. The four possible configurations of the C–O bond, taking account of the $\alpha\beta$-epimers, are shown in Fig. 3, and the corresponding infrared frequencies of the sterols in Table 2.

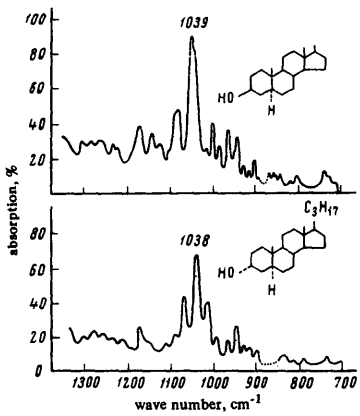


Figure 2. Infrared spectra of androstan-3β-ol and coprostan-3β-ol in the 700–1300 cm^{-1} range (see Cole and coworkers[19]).

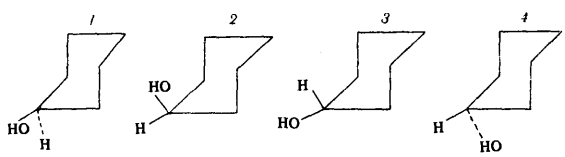
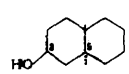
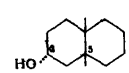
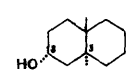
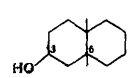
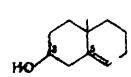


Figure 3. Four possible orientations of the C–O bond in the steroid molecules:
1) β-equatorial; *2*) β-polar; *3*) α-equatorial; *4*) α-polar.

Table 2. Frequencies of the C–OH stretching vibrations for various orientations of the OH group at $C_{(3)}$ and of the hydrogen atom at $C_{(5)}$ and various configurations of the C–O bond in sterol molecules[19].

Type of structure	A/B ring fusion	Configuration		Frequency range, cm^{-1}
		OH	C–O	
	*trans*	3β	equatorial	1037—1040
	*cis*	3α	equatorial	1037—1044
	*trans*	3α	polar	996—1002
	*cis*	3	polar	1032—1036
	Δ^5-double bond	3	equatorial	1050—1056

The frequency of the C–OH stretching vibrations is somewhat greater for the equatorial configuration. This is because an equatorial C–O bond causes some displacement of the $C_{(3)}$ atom along the C–O axis, which produces additional strain and compression of ring A, and this leads to an increase in the frequency of the C–O stretching vibrations. Nothing similar is observed for the polar configuration, since the stretching vibration of the C–O polar bond takes place mainly in the direction normal to the ring. Hence the investigation of the absorption in the range 950–1100 cm^{-1} can provide valuable information about the structure.

True, it must be mentioned that these authors[19] showed that it was possible for bands unconnected with a hydroxyl group to appear in the 1000–1100 cm^{-1} range, but their intensity is always lower. They usually appear for ketosteroids with a C=O group at the $C_{(17)}$, $C_{(7)}$, $C_{(11)}$, $C_{(12)}$, or $C_{(20)}$ carbon atom.

Yet another important work on this problem was published by Rosenkrantz and Scogstrom[20] in 1955. In it they investigated not only the most intense band in the 950–1100 cm^{-1} range but also a series of less intense and closely adjacent bands. Tetrahydrosteroids formed the subject of the investigation. The group of less intense bands situated close to the main band also seemed characteristic for the mutual arrangement of the substituents at $C_{(3)}$ and $C_{(5)}$. The authors[20] give the following results for the absorption of the C–O bond of the tetrahydrosteroids in dependence on the epimeric forms: 3α,5α 1005 cm^{-1}; 3β,5β 1035 cm^{-1}; 3α,5β 1041 cm^{-1}; 3β,5α 1044, 995, 978, and 956 cm^{-1}, depending on the structure of the rest of the molecule. The constant presence of a triplet band in the 3β,5α steroids was associated by the above authors with the possibility of the existence of three spatial orientations of the C–O bond. The possibility of using infrared spectroscopy for determining the spatial arrangement of the C–O bond of sterols was also demonstrated by Heller[21], who illustrated the determination of the polar and equatorial configurations by the example of 22 sterols. Page[22] undertook a similar study of other compounds of the sterol series.

In 1962 Rosenkrantz and coworkers[23] confirmed the earlier correlations by the example of thirteen 19-norsteroids. Unlike the previous studies the spectra of the 19-norsteroids were measured for the solid phase by the technique of the KBr disc. The authors obtained the following values for the infrared frequencies for the various isomeric forms of the 19-norsteroids: 3α,5α 998–1017 cm^{-1}, 3α,5β 1035–1060 cm^{-1}, 3β,5α 1042–1060 cm^{-1}, 3β,5β 1033–1055 cm^{-1}.

The band of the C–OH stretching vibrations is also sensitive to other structural factors. Thus, Meda[24] showed that the epoxide ring has an effect on the free OH group at $C_{(20)}$ but does not affect the absorption of an acetylated OH group in the same position. Jones and Roberts[25] studied the infrared spectrum of various hydroxysteroids. They found the frequencies of the C–O vibrations which characterise the location of the hydroxyl group in the steroid molecule. Jones and Roberts[25] obtained the following frequencies: for OH in the 3β-position and a Δ^5-double bond 1056–1047, 1025–1019, 989–978, 958–953 cm^{-1}; OH in the 17β-position 1059–1046 cm^{-1}; OH in the 20β-position 1100–1090 cm^{-1}; OH in the 20α-position 1016–1008 cm^{-1}. Both 20α,5α- and 20α,5β-steroids have a band in the 957–952 cm^{-1} range, but only the 20α, 5β-epimers are distinguished by a band between 962 and 965 cm^{-1}.

Important successes were achieved in investigating the infrared spectra of the steroidal acetates. Even in an early study of Furchgott[11] it was shown that the >C–O group gives a band for the C–O stretching vibrations close to 1250 cm^{-1}. Subsequently Jones and coworkers[26] studied the dependence of the absorption by the acetate group at $C_{(3)}$ on its *cis*- or *trans*-position in relation to a hydrogen atom at $C_{(5)}$. The decisive role in studying this subject is played by the number of bands of the acetate group (1190–1280 cm^{-1} range). An isolated band in the 1236–1247 cm^{-1} range is observed for all the compounds in which the acetate group at $C_{(3)}$ and the hydrogen at $C_{(5)}$ are in the *trans*-position and also for compounds with a Δ^5-double bond. In every instance when the acetate group occupies a 3β position *cis* to $C_{(5)}$ (3β,5β) there is a triplet band in the range 1200–1250 cm^{-1}. A less expressed triplet band is observed also for the 3α, *cis* to $C_{(5)}$ (3α,5α) configuration[26]. Each of the *trans*- and *cis*-forms has, of course, two stereoisomers, but the latter are readily distinguished by precipitation of the steroid with digitonin, which also determines the configuration at $C_{(3)}$. In another paper, Jones and Herling[27] investigated about 90 spectra of steroidal acetates, which confirmed their previous results. They suggest[26,27] that the reason for the observed differences in the absorption by the C–O bond of the *cis*- and *trans*-compounds is that the *cis*-compounds, which give three bands, can exist as mixtures of rotational isomers produced as a result of the delayed rotation of the acetate group around the C–O bond. As might be expected, when ring A is aromatic, there is a displacement of the band of the C–O stretching vibrations of the acetate group at $C_{(3)}$ to 1205 cm^{-1}.

The characteristic frequencies of the acetate group of steroids was also studied by Fürst and coworkers[28], who confirmed the presence of a triplet band for the 3α-acetoxysteriods. In addition to the 3-acetoxysteroids they investigated[28] the infrared spectra of sterols with acetate groups at $C_{(2)}$ and $C_{(4)}$. It is interesting that in this work[28] the authors ascribe the sterol band in the 1000–1100 cm^{-1} range not to the C–OH stretching vibration but to the deformation vibrations of the O–H bond. Fig. 4 shows the infrared spectra of the sterols and the corresponding acetates.

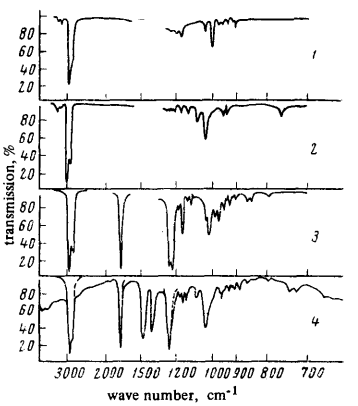


Figure 4. Infrared spectra of 3α-hydroxycholestane (1), 3β-hydroxycholestane (2), 3α-acetoxycholestane (3), and 3β-acetoxycholestane (4) in the 700–4000 cm^{-1} range (see Furst and coworkers[28]).

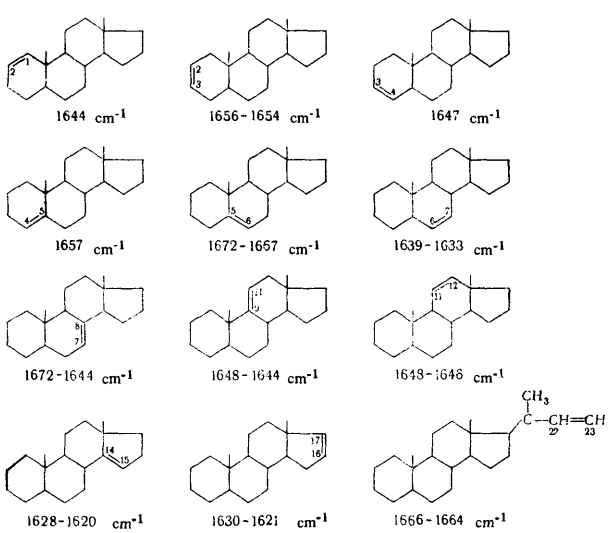
Rosenkrantz[20] obtained similar results, as later did Wotiz and coworkers[29] for 2,3,4-steroidal acetates. The same regularity of absorption was also observed for decanol acetates[30].

b. C=C Bonds

The band for the C=C stretching vibrations in the infrared spectrum is of weak intensity. Its intensity with symmetrical or pseudosymmetrical substitution is especially low. For ethylene and its symmetrical substituted derivatives this band generally does not appear, since it is forbidden by symmetry.

However, in the infrared spectra of such molecules as steroids, which have the lowest symmetry group, the band for the C=C stretching vibrations are sometimes rather sharp and can be suitable for structural conclusions.

Table 3. Frequencies of the C=C stretching vibrations as a function of the position of the C=C bond of the steroid molecule[31].



In the first studies on the infrared spectroscopy of the steroids[11-13] it was shown that the band of the C=C bond lies at 6.0 μm (1667 cm^{-1}) and the conjugation of the double bonds leads to the appearance of a band near 6.2 μm (1613 cm^{-1}). In the same studies[11-13] there were shown to be a difference in the frequencies of absorption by the C=C bond for differences in its position in the steroidal molecule: Δ^5 1671–1667 cm^{-1}, Δ^4 1610 cm^{-1}, Δ^{16} 1597 cm^{-1}, and when the Δ^4 double bond is conjugated with the carbonyl group at $C_{(3)}$ 1616 cm^{-1}.

Somewhat later Jones and coworkers[31] found a similar correlation between the frequency of the stretching vibrations of the C=C bond and its position in the molecule (Table 3).

In another investigation Jones and coworkers[32] confirm the absorption by the Δ^4-double bond of steroids in the 1612–1615 cm^{-1} range when there is a carbonyl group at $C_{(3)}$. The infrared spectra of steroids which contain Δ^5-, Δ^6-, Δ^7-, $\Delta^{5,7}$-, $\Delta^{8(14)}$-, $\Delta^{14(15)}$-double bonds were investigated by Jones and coworkers[33], who found that the compounds with Δ^5- and Δ^7-double bonds give a single weak band at 1600 cm^{-1}. The $\Delta^{5,7}$-sterols, which have two double bonds in conjugation, show two stronger bands at 1607 and 1625 cm^{-1}. Scheer and coworkers[34] found more accurately the characteristic frequencies of $\Delta^{5,7}$ conjugated bonds. They found three bands in the spectra of many steroids: 1575, 1603, and 1629–1624 cm^{-1}.

The dependence of the absorption of the C=C bond on its position in the triterpenoids was studied by Cole and Thornton[35].

The absorption of the Δ^4-double bond in 3,6-diketosteroids[36] lies between 1603 and 1609 cm^{-1}.

The paucity of results on the spectroscopic–structural correlations of the C=C bond is apparently due the the following causes: firstly, the presence and the nature of the double bond is easily found from the ultraviolet absorption spectra; secondly, when there is a hydrogen atom at an aromatic carbon atom the absorption of the stretching and out-of-plane deformation C–H vibrations of the $\rangle$C–H group is more sensitive to a change in structure than the absorption of the C=C bond itself; thirdly, the weak intensity of the band of the C=C stretching vibrations often creates additional difficulties in studying infrared spectra.

In conclusion we note that the band of the C=C stretching vibrations is always active in the Raman spectra. With non-symmetrical substitution the band of the C=C bond is more intense for the *cis*-isomer than the *trans*-isomer.

c. C=O Bonds

The high intensity, the isolated position in the infrared spectrum, and localised nature of the bands of the stretching vibrations of carbonyl groups makes these bands very convenient for spectroscopic investigations of structure. For the same reason the C=O bands are convenient for theoretical investigations of the dependence of the intensity of the bands on the redistribution of the charges in the molecule during the vibration process[37,38].

The keto-steroids have for the most part been studied from the empirical standpoint. The main problem in these investigations was whether a correlation exists between the number and position of the carbonyl groups and the corresponding absorption in the infrared spectrum, on the basis of an analysis of the spectra of keto-steroids with a known structure.

Significant success was attained in this study mainly thanks to the work of Norman Jones, whose investigations into the infrared spectroscopy of steroids can justifiably be considered classical. Earlier investigations of the infrared spectra of the steroids had shown that the frequency of the C=O stretching vibrations depends on the position of the C=O group in the keto-steroid molecule[11-13,39]. The following correlations were established in these studies:

$C_{(3)}$=O of steroids of the pregnane series	1739 cm^{-1},
$C_{(3)}$=O and Δ^4 double bond	1675–1672 cm^{-1},
$C_{(20)}$=O	1704–1712 cm^{-1},
$C_{(20)}$=O and Δ^{16} double bond	1675 cm^{-1}.

(the numbers at the carbon atoms show the numbers of the atoms according to the accepted numbering of carbon atoms in steroids).

Jones and coworkers[32] obtained more detailed information:

Nature of the bond		Frequency of the stretching vibrations, cm^{-1}	Number of examples
Non-conjugated	$C_{(3)}$=O	1717–1719	11
ditto	$C_{(20)}$=O	1706–1710	21
"	$C_{(17)}$=O	1742–1745	14
Conjugated	$C_{(3)}$=O	1674–1677	17
ditto	$C_{(20)}$=O	1666–1670	5

The diketo-steroids mainly have two bands, each of which corresponds to an individual C=O group[32].

In a later investigation Jones and another group of authors[40] completely confirmed the results of the previous work and also investigated some other keto-steroids. The following information was added:

Nature of the bond	Frequency of the stretching vibrations, cm^{-1}	Number of examples
Non-conjugated $C_{(11)}$=O	1710–1716	21
$C_{(7)}$=O	1719*	3
$C_{(12)}$=O	1710	2
Simultaneous presence of $C_{(11)}$=O and $C_{(17)}$=O	1751–1754	5
21-Acetoxy-group and $C_{(20)}$=O	1756–1758	4

* Rosenkrantz[15] obtained the same result later (17121 cm^{-1}).

Finally the generalising work of Jones and coworkers[41] appeared a year later (1950). The results of the previous studies were again confirmed and perhaps only some new results need be stated:

Nature of the bond	Frequency of the stretching vibrations, cm^{-1}	Number of examples
$C_{(16)}$=O	1745	5
$C_{(7)}$=O	1713–1714	7
$C_{(20)}$= and $C_{(21)}$-acetoxy	1756–1758	12
$C_{(6)}$=O	1713–1714	3
$C_{(12)}$=O and $\Delta^{9(11)}$-double bond	1680–1684	4

Approximately the same results were obtained later by Rosenkrantz and coworkers[16,20].

The carbonyl band of an acetate group in the side-chain of a steroid[40] appears at 1742 cm^{-1}, more rarely at 1739 cm^{-1}.

Replacement of a hydrogen atom close to a C=O group by halogen leads to a drop in the frequency of the C=O band[42], by 7 cm^{-1} for 17α-bromo-3β-hydroxy-5α-androstan-16-one, and by 17 cm^{-1} for the corresponding 17β-5α-epimer.

The carbonyl absorption of the steroids of the cholestane series which contain an acetate group was investigated by Fürst and coworkers[28]. Their results[28] suggest that irrespective of the position of the acetate group the carbonyl absorption of this group is strictly localised in the 1734–1740 cm^{-1} range. However, for the 3α- and 3β-acetates of the pregnane series Jones and coworkers[43] found the absorption of C=O between 1735 and 1732 cm^{-1} that is, somewhat lower.

Other results of Jones[44] and of Josien and coworkers[45,46] confirmed the correctness of the assignment of the carbonyl frequencies of the keto-steroids.

Depending on the molecular environment it seemed possible to characterise about 130 types of carbonyl systems of steroids according to their characteristic infrared frequencies. This work was carried out by Jones and Herling[47].

Bellamy and Williams[48], in studying the infrared spectra of keto-sterols noted that the frequencies of the C=O stretching vibrations of these substances are somewhat less (by 6–15 cm^{-1}). The authors[48] explained this by the formation of an intramolecular hydrogen bond C=O....HO. However, directly contradictory results were obtained by Jones and Robertson[49] for the 16,17-ketols of steroidal origin. In this work it was found that in the presence of hydroxy- and acetoxy-groups near to a C=O group there is an increase in the frequency of the C=O stretching vibrations by approximately 10 cm^{-1}. This problem apparently requires further precision.

The number of carbonyl groups could be determined by measurement of the integral intensities. By integral intensity is usually meant the total area bounded by the absorption band. For several monoketo-steroids the integral intensities of the C=O band were found by Jones and coworkers[50]. These results are given in Table 4.

Table 4. Integral intensities of the band of the C=O stretching vibration in the infrared spectra of monoketo-steroids[50].

Type of carbonyl group	Value of the integral intensity for various compounds, 10^4 litre $mole^{-1}$ cm^{12}	Mean value
C_3=O	2.63; 2.41; 2.39; 3.62;	2.55
C_7=O	2.17; 2.15	2.16
C_{12}=O	2.27	2.27
C_{17}=O	2.52; 2.72; 2.81; 2.64; 2.54; 2.91; 2.69	2.69
C_{20}=O	1.75; 1.84	1.80
C_3=O and Δ^4-double bond	2.88; 3.04; 3.67; 4.02; 3.39; 3.51; 3.67; 3.70; 4.11	3.65
Acetate group	3.15; 3.06; 3.14; 3.27; 3.39; 3.41	3.24

Then on starting from the integral intensities of the C=O band of the monoketosteroids, the integral intensities of the C=O absorption of the di- and poly-carbonyl steroids were calculated by an additive scheme. The results of these calculations and the directly observable integral intensities of some polyketosteroids are compared in Table 5.

Dvoryantseva and Sheinker[51] carried out a more concrete study, the aim of which was to determine the number of keto-groups in steroidal ketones.

Table 5. Integral intensities of the bands of the C=O stretching vibrations in the infrared spectra of di- and poly-carbonyl steroids[50].

Number and position of the carbonyl groups of the compounds	Infrared absorption maximum, cm^{-1}	Integral intensity of absorption, 10^4 litre $mole^{-1}$ cm^{-2}	
		calculated from the results in Table 4	observed
C_3=O and C_{17}=O	1719 1745	5.24	5.19
C_3=O and C_{20}=O	1719 1710	4.34	4.45
C_3=O; C_{20}=O and C_{12}=O	1712	6.61	6.93
C_3=O; C_{20}=O and Δ^4-double bond	1708 1677	5.44	5.90
3,20-diacetate	1739	6.48	6.21
3,16,20-triacetate	1739	9.72	9.05

The absorption of the carbonyl groups having various positions in the triterpene skeleton was studied by Cole and Thornton[35]. The effect on the absorption of the conjugation of a double bond with a C=O group was noted. In two papers of Tarpley and Vitiello[52] the influence of the solvent on the position of the bands of the C=O stretching vibrations in the infrared spectra of steroids was studied. The authors[52,53] measured 56 spectra in CS_2, CCl_4, $CHCl_3$, CH_2Br_2, and $CHBr_3$ solutions.

Recently a series of papers has appeared[54–59] on a study of the isotopic shift of the C=O frequency in the infrared

spectra on replacing ^{16}O by ^{18}O. In all instances a drop in frequency by 20–40 cm^{-1} is observed. Simultaneously there is an increase in the intensity of the displaced bands by ~20%.[59] The use of isotopic replacement of oxygen in keto-steroids could give interesting results in the near future.

As regards the other types of vibrations of the C=O bond, evidently they can also appear in the infrared spectrum. Thus Weinmann[60], by measuring the spectra of twenty-three 20-keto-steroids in the 450–800 cm^{-1} range, assigned the band between 588 and 597 cm^{-1} to C=O planar deformation vibrations. For a conjugated keto-group the frequency of this band is increased to 650–655 cm^{-1} and in the presence of an acetoxy-group at $C_{(21)}$ two bands are observed: at 604–600 and 640–648 cm^{-1}. The orientation of an acetoxygroup in steroid acetates was determined from the absorption in this range[61].

d. C–H Bonds

The C–H stretching vibrations appear in the infrared spectra of all organic compounds in the 2750–3100 cm^{-1} range. The bands of the vibrations of the C–H bonds of the methyl, methylene, and ethylene groups differ in frequency and can be differentiated in the infrared spectrum. Furthermore there is a series of different types of vibrations for the same bonds. Such different types of vibrations also differ in frequency. Fox and Martin[62,63] assigned the bands to different forms of C–H vibrations and the assignment was subsequently confirmed by other investigators[64–66].

The following frequencies of the C–H stretching vibrations were found for steroids: 2985, 3080 (for the $\rangle C{=}C{-}H$ structure), 2941 cm^{-1}.[11,12,32,33] The C–H bonds of the aromatic carbon atoms of steroids of the cholestane series give a band for C–H stretching vibrations at 3050 cm^{-1}.[33]

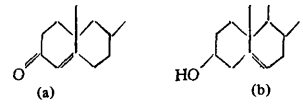
For the $\Delta^{4,6}$-3-keto steroids absorption analogous in nature is found at 3028 cm^{-1}, but for the Δ^{4}-3-keto steriods there is a weak band at 3034 cm^{-1}.

The increase in the frequency of the C–H stretching vibrations is a general phenomenon in the infrared spectra of polycyclic systems. Avram and coworkers[68] investigated this problem in detail, and in 27 polycyclic compounds found an increase in the frequency of the C–H stretching vibrations by 20–100 cm^{-1}. They thought[68] the reason for this is a change in the hybridisation of the electronic orbitals, which is expressed in the fact that the C–C bonds acquire a more and more marked p-character and the C–H bonds acquire an s-character, right up to sp^2 hybridisation.

Despite the fact that there is much information on the infrared spectra of steroids in the range of C–H stretching vibrations, these results do not give particularly valuable information about structure. However, from the absorption in the 2750–3100 cm^{-1} range methyl, methylene, and ethylene groups can be identified and by measuring the integral intensities the number of corresponding groups can be determined.

In studying the infrared spectra of steroids much more attention was and is being paid to the deformation vibrations of C–H bonds.

In even one of the first papers on the infrared spectroscopy of the steroids[7] it was shown that the ranges of the deformation vibrations of the methyl and methylene groups are respectively 1379–1389 and 1429–1481 cm^{-1}. The same investigation showed that steroids with structural formations of types (a) and (b) absorb at 870 and 840 cm^{-1} respectively (the range of the out-of-plane deformation vibrations of the ethylenic C–H bonds).



(a) (b)

Later this correlation was confirmed by other authors[15–16]. Jones and Cole specially considered[69] the problem of the absorption by methyl and methylene groups in steroid spectra. Their results are shown in Fig. 5, where the absorption by the methyl and the methylene groups of androstane are sharply differentiated. Hence their

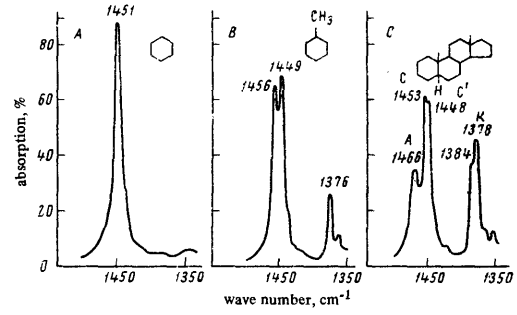


Figure 5. Infrared spectra in the range of the deformation vibrations of the methyl and methylene groups:
A) cyclohexane; *B*) methylcyclohexane; *C*) androstane[65].

results[69] show that the deformation vibrations of methylene groups give a band at ~ 1450 cm^{-1} and the angular methylene groups gives the doublet of bands at 1384 and 1378 cm^{-1} (confirmed by the spectra of many simple steroids which contain two angular methyl groups). However, their spectra of ten steroids which do not have a methyl group at $C_{(10)}$ (19-norsteroids) show a band only in the 1375–1378 cm^{-1} range. This observation allows the bands of the individual methyl groups to be identified:

CH_3 at $C_{(10)}$ 1375–1378 cm^{-1},
CH_3 at $C_{(13)}$ 1384 cm^{-1}.

We will quote some other correlations found by Jones and Cole[69]:

CH_2 group of keto-steroids	1400–1440 cm^{-1},
CH_2 group in a side-chain	1466–1469 cm^{-1},
CH_3 group in a side-chain attached to different atoms	1368 cm^{-1},
CH_3 group in a side-chain attached to a single atom	1380 cm^{-1},
CH_2 group of the cyclic part of the molecule	1448–1456 cm^{-1}.

In addition the authors investigated the region of absorption of an acetate methyl group (doublet band sensitive to the position of the acetate group in the molecule) and the effect of double bonds on the absorption of the methylene groups. Hence individual methyl and methylene groups of steroids could be identified from the infrared spectrum in the 1300–1500 cm^{-1} range. An example in this respect is the spectrum of 19-norpregn-4-en-3,20-dione (Fig. 6) which distinctly shows the absorption by different functional groups and even of the same functional groups found in different atomic environments. These results are confirmed in another paper[43] where the assignment of the bands is checked with the aid of selective deuteration. At about the same time Jones and coworkers[70] undertook the work of

assigning the bands in the infrared spectra of steroidal sapogenins. The range 1408–1435 cm^{-1} was given in a later work of Jones and coworkers[71] for absorption by the methylene group of the $CO-CH_2$ structure of $C_{(19)}$-keto-steroids.

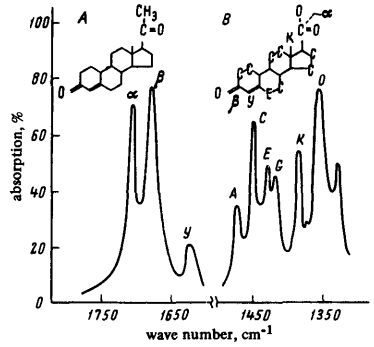


Figure 6. Infrared spectra of 19-norpregn-4-en-3,20-diol in the 1300–1800 cm^{-1} range[69]. *A*) and *C*) methylene groups of the cyclic part of the molecule at $C_{(1)}$, $C_{(7)}$, $C_{(11)}$, $C_{(12)}$ $C_{(14)}$, and $C_{(15)}$; *G*) methylene group at $C_{(2)}$ (influence of $C_{(3)}$=O); *E*) methylene group at $C_{(6)}$ (influence of Δ^4-double bond); *K*) angular methyl group at $C_{(13)}$; *O*) CH_3 at $C_{(21)}$ (characteristic frequency of the structure $H_3C-C=O$); α) and β) $C_{(3)}$=O and $C_{(20)}$=O keto-groups respectively; γ) $C_{(4)}=C_{(5)}$ double bond.

Much attention was paid to the absorption by C–H in unsaturated steroids. The deformation vibrations of the hydrogen atoms connected to aromatic carbon atoms occupy the range 650–1000 cm^{-1}, very sensitive to the molecular structure, in particular, to the location of the double bonds of the molecule. Thus for Δ^{22}-steroids which contain a double bond in the side-chain (ergosterol, vitamin D_2)[17,72], absorption in the 970–974 cm^{-1} range is characteristic. At the same time for steroids which do not have a Δ^{22}-double bond this band is absent (this is evident on comparing the spectra shown in Figs. 7–11).

The difference in the absorption of the C–H deformation vibrations for different positions of the double bond in steroids was found by Furchgott and coworkers[12,13]. Jones and coworkers[33], and then Hirschmann[73] investigated the spectra of steroids with Δ^5-, Δ^7-, or $\Delta^{5,7}$-double bonds in ring B. All the steroids with a Δ^5-double bond are characterised by a 798–803 cm^{-1} band. The $\Delta^{5,7}$-steroids have a characteristic doublet at 800 and 840 cm^{-1}. The Δ^7-steroids show only one band[33], at 835–840 cm^{-1}. Evidently the band at 800 cm^{-1} is from the $C_{(6)}$–H bond and the band at 835–840 cm^{-1} from the $C_{(7)}$–H bond.

Jonson and coworkers[33] also studied the influence on the absorption in this region of the hydroxy- and acetoxy-groups at $C_{(3)}$ and found a characteristic doublet for 3-acetoxy-Δ^4-steroids at 800 and 812–815 cm^{-1}.

The same results in assigning the bands in the infrared spectra of the steroids in the 700–1000 cm^{-1} range were obtained by authors of both earlier[74,75] and later[34,76,77] studies.

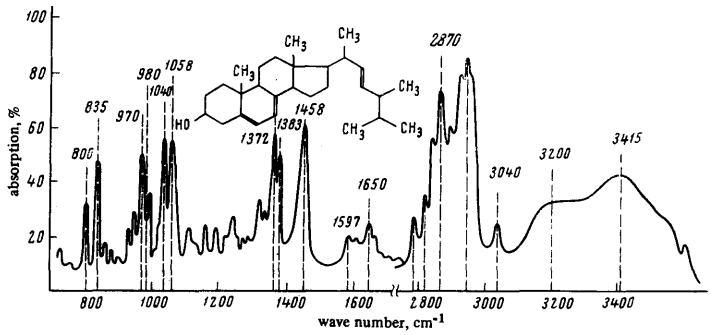


Figure 7. Infrared spectrum of the provitamin D_2 (ergosterol) in the range 700–1400 cm^{-1}.

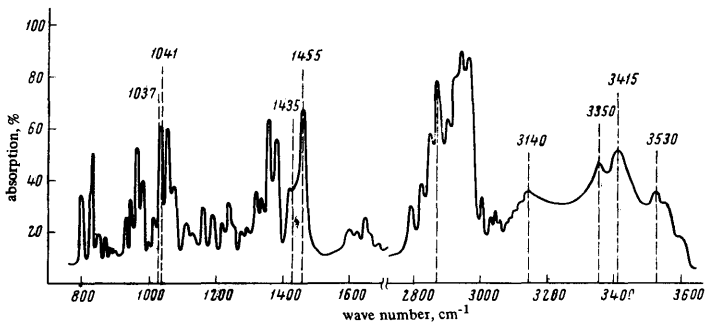


Figure 8. Infrared spectrum of ergosterol in the 700–4000 cm^{-1} range at -183°C.

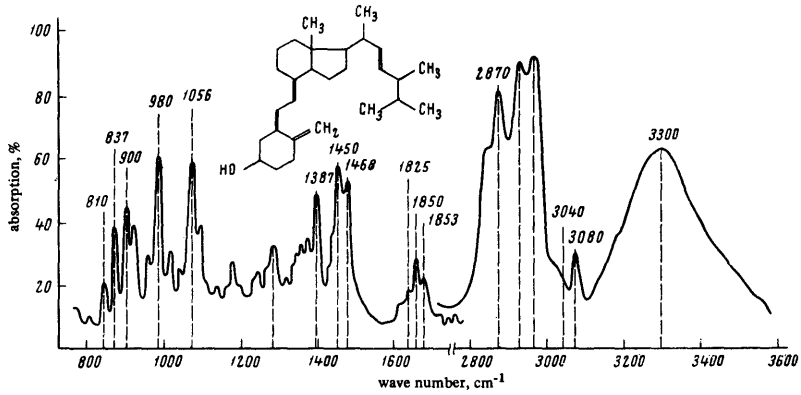


Figure 9. Infrared spectrum of vitamin D_2 in the 700–4000 cm^{-1} range.

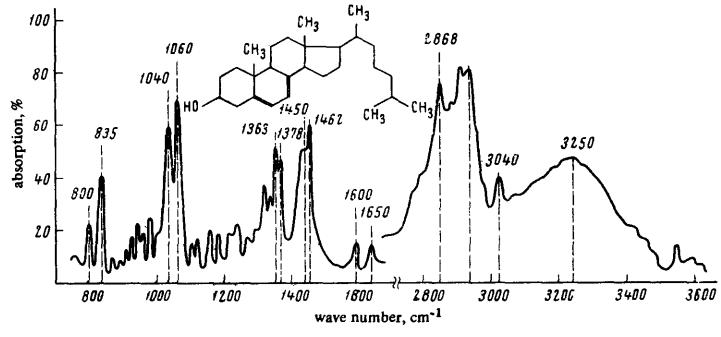


Figure 10. Infrared spectrum of the provitamin D_3 (7-dehydrocholestane) in the 700–4000 cm^{-1} range.

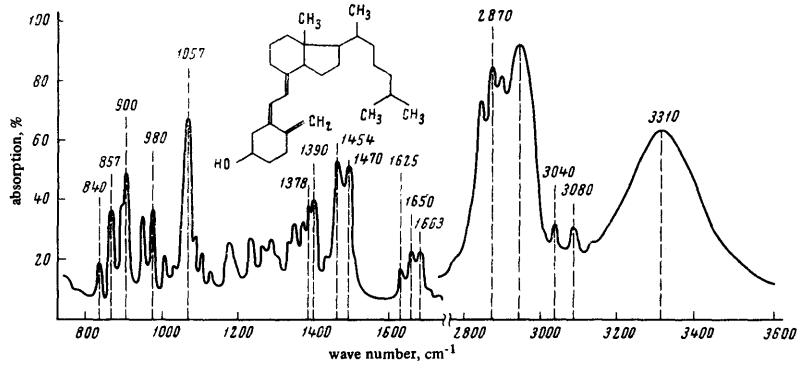


Figure 11. Infrared spectrum of vitamin D_3 in the 700–4000 cm^{-1} range.

When an ethylene bond is conjugated with a carbonyl group, the frequency of the C–H out-of-plane deformation vibrations is raised to the 867–904 cm^{-1} range[78].

Meda and coworkers[79] found a characteristic band in the 860–847 cm^{-1} range for pregn-4-en-16,17epoxy-steroids. This band can be assigned to the out-of-plane deformation vibrations of the $C_{(4)}$–H bond, but Meda and coworkers[79] evidently hold another opinion, since this band is proposed by them for the identification of the epoxy-group.

e. O–H Bonds

Free hydroxyl groups of alcohols in solutions are responsible for the appearance of a narrow absorption band in the 3610–3636 cm^{-1} range. For hydroxy-steroids the region of absorption of the O–H stretching vibrations is rather variable and depends considerably on structure and on the nature of the intermolecular interaction. Furchgott and coworkers[11] found the absorption of the O–H stretching

vibrations at 3597–3344 cm^{-1} for the steroids which they investigated. For the hydroxy-steroids of the pregnane series the same authors give a somewhat different region: 3572–3448 cm^{-1}. Rosenkrantz and Zabloy[14] found a band for O–H stretching vibrations of steroids at 3679 cm^{-1} and showed that a change in solvent can lead to a displacement of the band to 3445 cm^{-1}.

For cholestanol derivatives Jones and coworkers[33] observed the band of the free OH group at 3620 cm^{-1}.

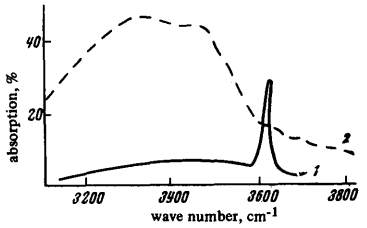


Figure 12. Infrared spectrum of ergosterol in the range of the stretching vibrations of the O–H bond: *1*) solution in CCl_4; *2*) solid phase.

In studying steroids with an aromatic ring A, Pickering and Werbin[77] found that an OH group at $C_{(3)}$ gives a band for O–H stretching vibrations at 3230–3335 cm^{-1}, and on OH group at $C_{(17)}$, one at 3415 cm^{-1}.

Dalton and coworkers[80] observed an increase in the splitting of the absorption bands of the O–H stretching vibrations from a slight shoulder for C_2H_5OH to a well differentiated band of almost equal intensity for 5α-cholestanol. It is suggested[80] that such a splitting occurs thanks to the conformational complexity of the structure of the molecule.

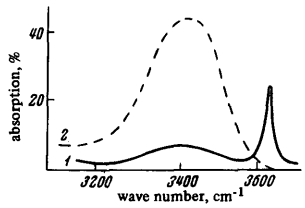


Figure 13. Infrared spectrum of 7-dehydrocholesterol in the range of the O–H stretching vibrations: *1*) solution in CCl_4; *2*) solid phase.

The influence of solvent on the frequency of the O–H stretching vibrations in the infrared spectra of the steroids was studied by Horak and Faikos[81]. The authors of the present review observed that for steroids the band of the free hydroxyl group lies at 3620 cm^{-1}. However, it can only be detected in the spectra for solutions where the molecules of the sterols are in monomeric form. In the spectra of the solid phase this band is absent, but a broad intense band appears between 3100 and 3600 cm^{-1}, due to intermolecular hydrogen bonds (Figs. 12 and 13). Hence the formation of large associates of molecules maintained by hydrogen bonds are inherent for steroids in the crystalline state. In addition to OH groups, the π-electrons of double bonds can participate in the formation of double bonds, for the spectroscopic manifestation of a hydrogen bond in the spectra of crystalline sterols which contain different numbers of C=C bonds is different. The structure of the hydrogen bond band (Fig. 8) is resolved in spectra at low temperature (–183 °C), showing that several types of intermolecular aggregation are realised simultaneously.

f. C–C Bonds and Large Fragments of Molecules

The bands of the stretching vibrations of simple carbon–carbon bonds are of low intensity and lie in the infrared spectrum below 1200 cm^{-1}. The general regularity of the absorption in this region was investigated by Brown and coworkers[82]. The possibility of the use of the band for the C–C stretching vibrations in studies of structure was investigated by McMurry and Thornton[83].

Jones and coworkers[76] found the frequency of the skeletal vibrations which characterise two different structural types of keto-steroids. Josien and coworkers assign the bands at 794 and at 811 cm^{-1} to the vibrations of the cyclopentane ring of 3,5-methylenesteroids.

The band for the deformation vibrations of the C=C bonds lies in the infrared spectrum below 600 cm^{-1} and has not yet found a use in structural spectroscopy.

III. USE OF INFRARED SPECTROSCOPY IN STEROID CHEMISTRY

In most studies of the infrared spectra of steroids carried out up to the 1950's only the nature of the absorption and the known structure of the molecule were connected.

The results on the infrared spectroscopy of steroids have been surveyed in atlases of spectra[85,86], repeatedly checked. The spectroscopic–structural correlations which have been deduced and repeatedly confirmed have enabled molecules of unknown structures to be introduced into the field of the infrared spectroscopy of steroids. Hence since the 1950's infrared spectroscopy has been widely used for revealing the most varied problems of the structure of natural steroids and their synthetic analogues. The examples cited below illustrate the great possibilities and occasionally the necessity of using infrared spectroscopy in investigating the structure and conversions of the steroids.

1. Sterols

The most diverse problems of the steroid chemistry have been solved by analysis of their infrared spectra. Information on the absorption by the hydroxyl groups of sterols has appeared in Soviet[87] and foreign[88] literature.

Specific absorption of the OH groups is observed in the spectra of the cardenolides[89] and glycosides[90]. The infrared spectra of the sterols are used both for identification and for solving structural problems[92]. Thus Fudge and coworkers[93] used the infrared spectra for finding the structure of 5-hydroxy-derivatives of cholestane[93]. The results from molecular spectroscopy were used to determine the orientation of the hydroxyl group itself in molecules of natural sterols[94] and also for investigating the structure of cerebrosterol[95], 20-ketosteroid-3,11-diols[96], lanosterol and its derivatives[97,98], β-spinasterol[99], and derivatives of ergosterol[100].

The hydroxyl groups of steroids are capable of forming both intramolecular and intermolecular hydrogen bonds. From the infrared spectroscopy results the presence of intramolecular hydrogen bonds in 7-hydroxycholesterol was established between the 3-OH and 7-OH hydroxyl groups[101] and in steroidal 3,5-*cis*-diols between the 3-OH and 5-OH hydroxyl groups[102] (there are no hydrogen bonds in the 3,5-*trans*-diols), and in cholesterol and epicholesterol between the OH groups and the π-electrons of the double bonds[103].

Bernstein and coworkers[104] used infrared spectra to study 7α-hydroxysteroids. Infrared spectroscopy has been widely used in the investigation of steroidal diols[105-109] and triols[110-112], and also new sterols[113].

Infrared spectra were used successfully to study the structure and conversions of sterols of un-natural conformation, particularly lumisterol[114-117], which is an important intermediate in the photosynthesis of the vitamins of group D.

2. Unsaturated Steroids

In studying the unsaturated steroids the infrared spectra in the ranges 700–1000 cm^{-1} ($\gtrless$C–H out-of-plane deformation vibrations) and 1550–1650 cm^{-1} (C=C stretching vibrations) are used.

The presence and position of C=C double bonds was shown by infrared spectra for derivatives of allopregn-6-ene[118], Δ^{11}-unsaturated steroids[119], and 1-dehydrosteroids[120]. Levin and coworkers[121] studied the conformation of $\Delta^{5(10)}$-unsaturated steroids. The infrared spectra found application for studying the structure and conversions of steroidal hormones[122-126], derivatives of vitamin D_2,[127] $\Delta^{5,7}$-steroids[128,129], and steroids with an aromatic ring A.[130] Elks[131], and also Henbest and Wilson[132] studied steroidal trienes. Bergman investigated the infrared spectra with the aim of identifying C=C bonds in the side-chain of 22-, 24-, and 25-dehydro-derivatives of cholesterol[133,134]. The results of molecular spectroscopy were used to study the conformation of the D rings in Δ^{14}-unsaturated steroids[135]. Absorption in the 700–1000 cm^{-1} range was used to find certain features of the structure of $\Delta^{3,5}$-steroids[136]. Information has also been obtained about the spectra of synthetic steroidal hormones[137] and their derivatives[138].

3. Steroidal Ketones

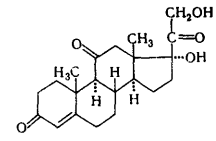
The infrared spectra of steroidal ketones have been widely used both for the identification[139-141] and for elucidating the structure[142-145] of steroids. The principal task of these spectroscopic investigations was naturally to find the presence and position of the carbonyl groups. In the chemistry of steroidal ketones infrared spectra are usually the main test of an investigation of the structure and of the mechanism of chemical reactions in which C=O groups participate.

Infrared spectra are used successfully in studying 3-keto-steroids[146-148], 7-keto-steroids[149], the conversions of 11-keto-steroids[150-152], and 15- and 20-keto-steroids of the pregnane series[153].

The results from infrared spectroscopy allowed the isomerisation of unsaturated ketones to be observed[154] and also the structure and conversions of various steroidal diketones to be investigated[155-161].

On the basis of the results of infrared spectroscopy, Baron and le Boulch[162] studied the structure of intermediate products between cholesterol and the "ketone 250" known in steroid chemistry.

Cortisone (IV) occupies a special place in the chemistry of steroidal ketones—it is the most important of the corticosteroidal hormones. After the discovery of the therapeutic action of this hormone intensive attempts to synthesise cortisone and its analogues were made.

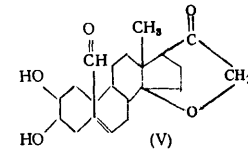


(IV)

In many of these studies the results from infrared spectroscopy of cortisone itself[163] and of its derivatives[164-167] were used fruitfully. With the aid of infrared spectra certain problems in the synthesis of cortisone were solved[168-171], and in particular the problems of the structure of intermediates in the synthesis[172,173].

4. Epoxysteroids and Lactones

In 1953 Gunthard and coworkers[174] proposed a method of distinguishing the stereoisomers of steroidal epoxides by their infrared spectra. Later with the aid of infrared spectroscopy features in the structure of steroids containing a seven-membered lactone ring were established[175]. On the basis of a study of infrared spectra, the structure of digifologenin[176] (V) together with certain other steroids having a five-membered lactone ring as ring D was established.



(V)

Many studies have employed infrared spectra to draw conclusions about the structure of other steroidal lactones[177-182] and epoxysteroids[183-188]. Infrared spectra have also been used to establish the structure of new synthesised lactones[189-191] and epoxysteroids[192]. Henbest and Wrigley[193] studied the reaction of 5,6-epoxysteroids with the complex $BF_3.Et_2O$ on the basis of the results from infrared spectroscopy. A large number of results from infrared spectroscopy was used for solving the problems of the synthesis of an important hormone of adrenal cortices—aldosterone[194-200]. Several studies were also devoted to the infrared spectra of steroidal sapogenins[201-209].

5. Methyl- and Methylene-steroids. Steroidal Acetates

Steroids which contain methyl and methylene groups as angular substituents and substituents in side-chains are conveniently investigated by the methods of molecular spectroscopy thanks to the specific absorption by these functional groups.

Certain structural aspects of this type of absorption were considered in Cole's review[210]. The problems of the structure of 3-methylcholestanol and its photo-derivatives was considered by Barton and coworkers[211]. Several authors give information about the infrared spectra of steroids which contain methyl substituents in the most varied positions in relation to the steroidal skeleton of the molecule: 6,[212,213] 7,[214] 16,[215,216] 20,[217] 9α,[218] 17α,[219,220]

17β,[221] 4α,[222] etc. There are also spectrographic results used in studying dimethyl-[223-225] and methylene-[226,227] steroids.

Since the infrared frequencies of the acetate group are sensitive to its stereochemical location in the molecule, the infrared spectra are often used in studying the structure[228-230], synthesis (acetylated derivatives of cortisone[231-233]), and conversions[234,235] of steroidal acetates and diacetates[236].

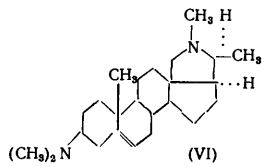
6. Halogenosteroids

The infrared spectra of the bromo-derivatives of steroids have been studied best, those of the iodo-derivatives worst. However, this is not paradoxical, the earliest information concerns iodosteroids; from an analysis of infrared spectra Djerassi and Lenk[237] proved the structure of intermediates in the synthesis of 21-iodo-Δ^{16}-20-ketosteroids. Infrared spectroscopy was used to investigate the bromination of sapogenins[238], bromosteroids of the cholane[239] and androstane[240] series, the configuration of the $C_{(17)}$ substituents in 16-ketoandrostan-6-ol[241]†, the conversion of 17α-acetoxy-16β-bromo-20-ketosteroids[242], the mechanism of bromination of keto-steroids[243-244] and certain other problems[245-247].

The infrared spectra of fluorosteroids have also been fairly well studied[248-253]. Less information is available on the infrared spectroscopy of chloro-steroids[254-256].

7. Nitrogen-Containing Steroids

Nitrogen enters into the composition of the molecule of many natural and modified steroids. It can be found in the steroids both as hetero-atoms in the rings and in the composition of various groups of angular substituents. A good example is conessine (VI), the infrared spectrum and structure of which were investigated by Phillips and Johnson[257].



(VI)

Results from infrared spectroscopy were also used in studying the synthesis of conessimine from conessine[258]. The infrared spectra of nitrogen-containing steroids were characterised by various chromophores, including nitrogen atoms: imine[259] (>C=NH–) 1638 cm^{-1} diazochromophores[260] ($-\overset{+}{N}=N-$) 2080 cm^{-1}, and the cyano- (nitrile-) chromophore[261-263] (–C≡N–) 2237 cm^{-1}.

The molecular spectra of nitrogen-containing steroids have now been reliably interpreted and are used in investigations of aza-steroids[264-267] nitro-steroids[268-270], amino-steroids[271], and hydroxyiminocholane acids[272].

8. Conversions of Steroids

Various changes in the structure of steroids are positively reflected in the infrared spectra. This disclosed the possibility of judging the converions of steroids from the changes in their infrared spectra. The results of this nature are available for steroids modified in the most diverse ways.

Thus Bladon and coworkers[273] observed a change in the infrared spectra of steroids subjected to reduction with sodium amalgam. Several studies are devoted to the infrared spectra of steroids modified by photochemical action[274-277].

Shoppee and coworkers often used infrared spectroscopy in a series of studies they made into the Walden inversion in reactions of compounds of a steroidal nature[278-280]. Infrared spectroscopy has been extensively used in studying the most varied conversions of steroids brought about by micro-organisms[281-291].

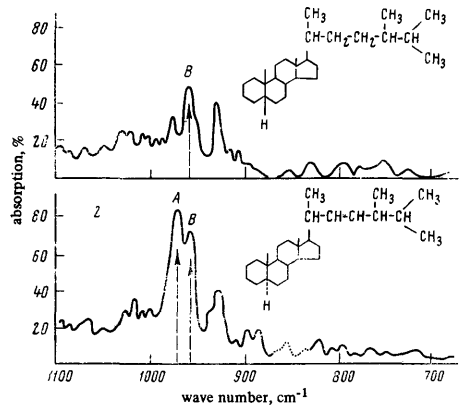


Figure 14. Infrared spectra of ergostane (1) and of ergost-22-ene (2) in the 700–1300 cm^{-1} range[168].

9. Some Particular Structural Problems

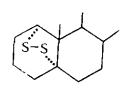
Infrared spectroscopy has been used successfully to solve some particular problems of structure, conversions, and metabolism of steroids.

The first of such studies were made by Jones as long ago as 1950.[72] In it, the absorption in the range 970–974 cm^{-1} showed that for ergost-22-ene the side-chain in $C_{(17)}$ steroids which contain a Δ^{22}-double bond has a *trans*-configuration relative to this bond (Fig. 14). For the *cis*-configuration absorption took place in the 670–800 cm^{-1} range.

Taub and coworkers[292] studied the side chain of corticosteroids from the absorption in the infrared range. Dobriner and coworkers[293] studied the metabolism of previously deuterated steroids from the band of the C–D stretching vibrations in the 2145–2165 cm^{-1}.

On the basis of infrared spectra Mateos and Chao[294] determined the form of ring D in certain steroid molecules.

Tweit and Dobson investigated the spectra of steroids with a trans-annular S–S bridge (VII) in ring A[295]:



(VII)

† This reference (241) does not mention 16-ketoandrostan-6-ol nor infrared spectroscopy! (Ed. of Translation).

Information on absorption in the infrared range of the spectrum was used in studying the structure of the most varied steroids, in particular, digacetinin[296], kitigenin[297], β-anhydrogromphogenin[298], steroidal nucleotides[299], steroidal glucosides[300-302], stereoisomers of prednizolone[303], and steroids with a butenolide ring[304,305]. An atlas of infrared spectra was recently published[306] which contains, in addition to the spectra of coumarins, flavonoids, and anthraquinones, 44 spectra of cardenolides—steroids which exhibit a butenolide ring. The infrared spectra have also found application in studying natural 24-alkyl steroids[307] and steroids isolated from marine products[308,309].

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In conclusion it should be noted that the material surveyed in the present review far from exhausts the possibilities of the infrared spectroscopy of steroids. In addition to the structural aspect and identification, infrared spectroscopy can be used for other purposes. However, the space for the present review does not permit consideration of all possible applications of the molecular spectroscopy of steroids.

In recent years the chemistry of steroids has been enriched by physical methods of investigation. Many authors employ in their investigation not only infrared spectroscopy but also the results of ultraviolet spectroscopy, optical rotatory dispersion, and circular dichroism, and electron paramagnetic and nuclear magnetic resonance. However, the value of the infrared spectra of the steroids is not diminished by this, since the combined use of all the above physical methods of studying structure gives, of course, a considerably more detailed information about steroid molecules than any method used in isolation.

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Organoelementary Derivatives of Barenes (Carboranes-10)

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CONTENTS

I.	Introduction	173
II.	Magnesium and alkali-metal derivatives; syntheses based on them	174
III.	Barenyl derivatives of boron	177
IV.	Derivatives of Group IV elements	178
V.	Derivatives of Group V elements (phosphorus, arsenic, antimony)	179
VI.	Mercury derivatives	180
VII.	Organometallic derivatives of dicarbaundecaborane	182

I. INTRODUCTION

One of the most surprising peculiarities of the icosahedral system of barene (carborane-10) and neobarene† is the unusual valency state of the two carbon atoms, each of which is bound simultaneously to six other atoms (Fig. 1).

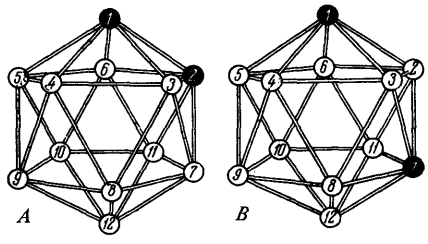


Figure 1. Structure of: *A*) barene; *B*) neobarene.

† The American name for barene is 1,2-dicarbaclovododecaborane-12, carborane-10, or ortho-carborane; neobarene is termed by them neocarborane or meta-carborane. For further details on the nomenclature of the barenes see Ref.1.

This fact, coupled with the strong electron-acceptor properties of the barene cage and the steric hindrance which it creates, makes the study of *C*-functional derivatives of barene extremely interesting. From the point of view of organoelementary chemistry the greatest interest attaches to derivatives containing a direct bond between the element and a cage carbon atom. The investigation of such compounds can obviously give valuable information on the nature and properties of the element–carbon bond in general.

The first papers reporting the discovery of barenes appeared at the end of 1963.[2-5]. A general method for synthesising them consists in the reaction of decaborane with acetylenes in the presence of Lewis bases:

$$B_{10}H_{14} + RC{\equiv}CR' \xrightarrow{L} RC\!-\!CR' + 2H_2$$

(the product is bonded to $B_{10}H_{10}$)

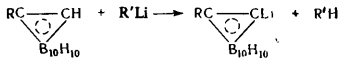
The chemical structure of barene, established theoretically by Lipscomb[6], was confirmed by X-ray[7-10] and electron[11] diffraction, although the first X-ray results subsequently proved to be erroneous[2]. The ten boron atoms and two carbon atoms of barene form an almost regular icosahedron (with interatomic distances C–C = 1.64–1.70 Å, B–C = 1.70–1.71 Å, and B–B = 1.70–1.79 Å), the C–C

bond length having no analogy throughout organic chemistry.

Barenes, in contrast to the original hydroboron, are stable towards oxidising agents, alcohols, strong acids, and bases, and possess phenomenal thermal stability. At 500°C barene isomerises into neobarene, in which the two carbon atoms are in the "meta" position relative to one another[12,13]. The chemical properties of barenes have recently been reviewed by Issleib et al.[14], and therefore we shall henceforward consider only those which are significant for the present paper. The most important of these properties is the "acidic" character of the C–H bonds, as a consequence of which the protons attached to the carbon atoms can be fairly easily replaced by alkali metals when the barenes are treated with the amides or lithium alkyls.

II. MAGNESIUM AND ALKALI-METAL DERIVATIVES; SYNTHESES BASED ON THEM

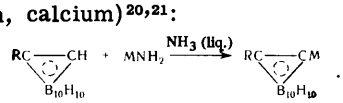
Organolithium derivatives of barenes, which are widely used for the synthesis of various barenyl compounds, are readily obtained by the action of butyl-lithium[15–17] or phenyl-lithium[16–18] both on barene itself and on monoalkyl- and monoaryl-barenes:



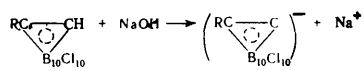
The reaction is usually accomplished by treating the barenes with a benzene solution of butyl-lithium at 60–80°C.[15]

To obtain the monolithium derivative of barene itself, the reaction must be conducted in ether at 0°C, and the solution of n-butyl-lithium or phenyl-lithium added to the barene in such a manner that excess of the latter is present throughout the reaction[16]. In contrast to this, the addition of an ethereal solution of barene to excess of n-butyl-lithium at 0–15°C results in a good yield of dilithiumbarene[16]. This derivative is obtained also by the action of excess of n-butyl-lithium in heptane or pentane on barene in tetrahydrofuran and of phenyl-lithium on barene in ether[17]. Neobarene undergoes methylation under similar conditions[12].

The sodium derivatives of barenes, the possibility of whose synthesis by the action of sodamide on the corresponding barenes was shown by Zakharkin et al.[19], are of great value for preparative purposes. This reaction was subsequently extended to the amides of other metals (lithium, potassium, calcium)[20,21]:

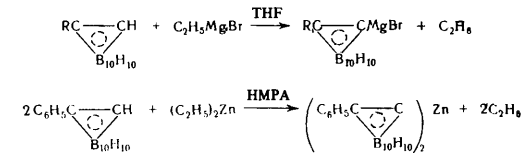


The ease of metallation of barenes by metal amides and lithium alkyls indicates the acidic character of the hydrogen atoms attached to the carbon atoms of the barene cage, this being due to the strong electron-acceptor action of the cage. Replacement by chlorine atoms of the hydrogen atoms attached to boron reinforces the electron-acceptor effect of the barene cage. The acidity of the decachlorobarenes has increased so much that they are now actual proton acids, which should dissolve in weak aqueous solutions of alkalis to give the corresponding sodium derivatives in the completely ionised state[22]:



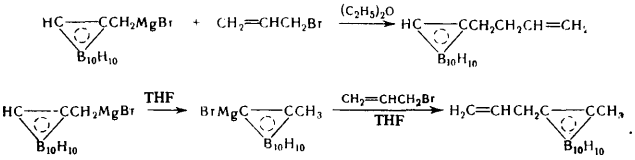
where R = H, C_6H_5.

In contrast to the reactions with lithium alkyls and metal amides, however, the hydrogen atoms attached to the carbon atoms of the barene cage are not replaced by a metal atom on treatment with organomagnesium and organozinc compounds in ethereal medium. The reaction goes only when complexing solvents are used. Thus ethylmagnesium bromide reacts smoothly with barene, methylbarene[17], and neobarene[23] in tetrahydrofuran (THF) medium, and diethylzinc reacts with phenylbarene in hexamethylphosphoramide (HMPA) medium[24]:

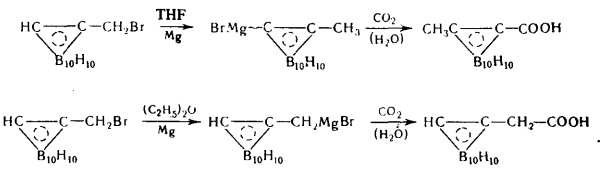


where R = H, CH_3.

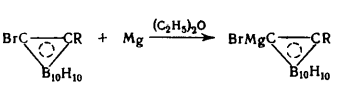
An interesting reaction was discovered by a group of American chemists[17] when preparing a Grignard reagent from bromomethylbarene. It was found that in tetrahydrofuran (unlike ether) the barenylmethylmagnesium bromide underwent isomerisation, and on treatment with allyl bromide gave 1-allyl-2-methylbarene instead of 4-barenylbut-1-ene:



The occurrence of such isomerisation was confirmed by Stanko[25], who showed that carboxylation in tetrahydrofuran of the Grignard reagent obtained from bromomethylbarene yielded methylbarenecarboxylic acid. When the reaction was conducted in ether, barenylacetic acid was formed:



Barenylmagnesium halides were obtained also directly from compounds containing a cage carbon–halogen bond:



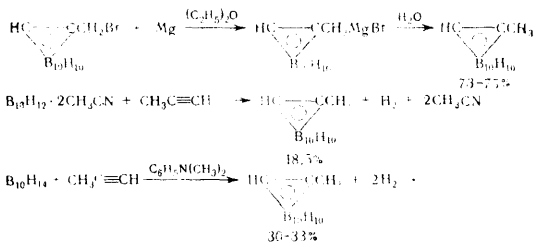
where R = n-C_3H_7, n-C_4H_9. However, these compounds did not react with aldehydes or ketones[16]‡.

The ease with which barenyl derivatives of elements in Groups I and II can be obtained has enabled a large number of diverse barenyl compounds to be synthesised on their basis.

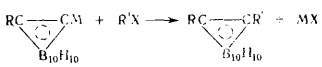
The carboxylation of barenylmethylmagnesium bromide mentioned above provides a more convenient method for preparing barenylacetic acid than synthesis from decaborane and ethyl but-3-ynoate[25]. Formation of methylbarene by the hydrolysis of barenylmethylmagnesium bromide occurs with a far better yield[16,26] than is obtained by the

‡ It has recently been reported[87] that analogous Grignard reagents, containing hydrogen, methyl, vinyl, and phenyl as substituents, react readily with aldehydes and ketones, as well as with alkyl halides[88].

reaction of propyne with decaborane in the presence of a Lewis base[27,28]:

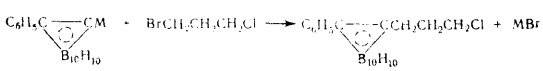


The alkylation of *C*-metal derivatives of barenes was investigated by several American chemists[12,16-18,29,30], and has subsequently been subjected to detailed study by Zakharkin and Kazantsev. They have synthesised a large number of alkyl and aryl derivatives of barene[20,21,31] and neobarene[32] on the basis of the reaction



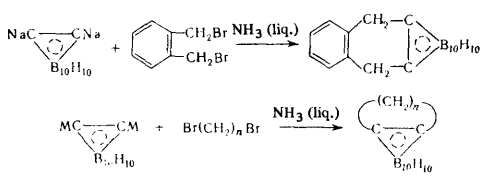
where M = Li, Na, K.

It is more convenient to work with sodium derivatives in liquid ammonia than with lithium derivatives in benzene or ether. Primary alkyl bromides and iodides, alkenyl bromides, $\alpha\omega$-dibromoalkanes (other than 1,2-dibromoethane), chloro-derivatives such as benzyl chloride, and dialkyl sulphates react smoothly. Primary alkyl chlorides react extremely slowly with metal derivatives of the barenes, and this permits the selective alkylation of the *C*-metal derivatives by $\alpha\omega$-bromochloroalkanes with the formation of α-barenyl-ω-chloroalkanes[31]:

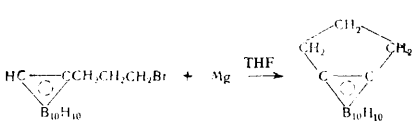


where M = Li, Na.

With secondary and tertiary alkyl bromides practically no alkyl derivatives are formed[31]. Barene derivatives containing two metal atoms react with certain $\alpha\omega$-dihalogeno-derivatives to give five- and six-membered carbocyclic compounds[31,33]:

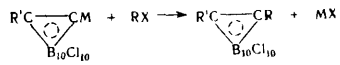


where M = Na, K and n = 3, 4. An analogous five-membered cyclic derivative is formed when an attempt is made to prepare a Grignard reagent from barenylpropyl bromide[34]:

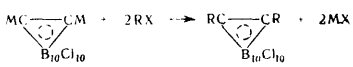


Such cyclisation is explained by metallation by the resulting Grignard reagent of another molecule of the halogenated barene followed by elimination of magnesium bromide.

C-Alkylation of *B*-decachlorobarene goes smoothly by the action of alkyl halides either on lithium salts of decachlorobarene in ethereal or toluene medium[35] or on the analogous sodium derivatives in alcoholic or aqueous-alcoholic medium[36]:



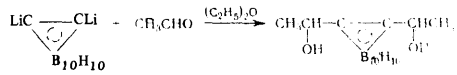
where M = Li, R = CH_3, C_2H_5, R′ = H, X = I;
or M = Na, R = CH_3, R′ = C_2H_5, X = I;
R = C_2H_5, R′ = H, X = I;
R = CH_2 : $CH.CH_2$, R′ = H, X = Br;
R = $C_6H_5.CH_2$, R′ = H, X = Cl;



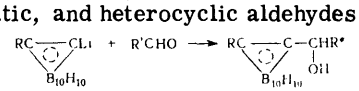
(M = Li, R = CH_3, C_2H_5, X = I or M = Na, R = CH_3, X = I).

The lithium derivatives of barene readily react with various aldehydes, from which alcohols can be obtained containing the hydroxyl in the α-position with respect to a carbon atom of the barene cage[20,21,37,38].

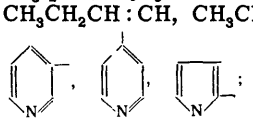
Heying et al.[16], who were the first to accomplish a reaction of this type, used dilithiumbarene, from which the corresponding diol was obtained by reaction with acetaldehyde:



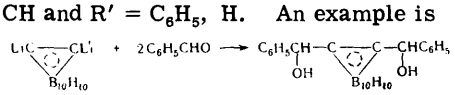
This reaction was subsequently extended to several aliphatic, aromatic, and heterocyclic aldehydes[37,38]:



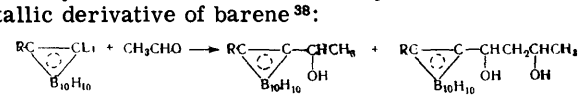
where R = CH_3, $(CH_3)_2CH$, C_6H_5 and R′ = C_6H_5; R = CH_3, C_6H_5 and R′ = H, $CH_3CH_2CH:CH$, $CH_3CH:CH$, *p*-$CH_3OC_6H_4$ *o*-ClC_6H_4,



R = $CH_2:CH$ and R′ = C_6H_5, H. An example is

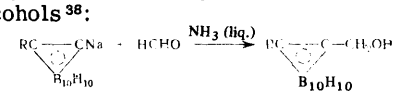


Reaction of lithiumbarenes with acetaldehyde may result not only in the normal reaction product—a secondary alcohol—but also in a diol, a product of the reaction of lithiumbarene with β-hydroxybutyraldehyde, which is probably formed by the action of the secondary alkoxide or a *C*-metallic derivative of barene[38]:

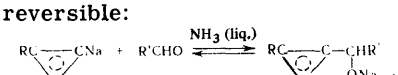


where R = CH_3, C_6H_5.

Sodium derivatives of barenes in liquid ammonia react smoothly only with formaldehyde, to give 92–94% yield of primary alcohols[38]:

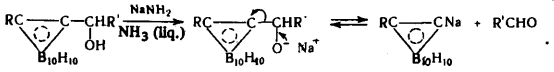


where R = CH_3, C_6H_5. With other aldehydes the yields were substantially lower, mainly because the reaction of sodium derivatives of barenes with aldehydes in liquid ammonia is reversible:

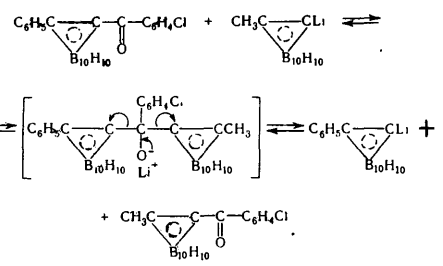


This phenomenon is probably a particular case of the general tendency of the carbon–carbon bond in carbonyl derivatives and alcohols of the barene series to undergo

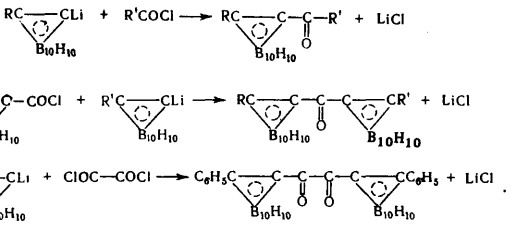
cleavage in the presence of bases[39-41], which is explained by the strong electron-acceptor effect of the barene cage:



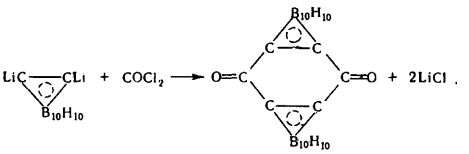
An analogous explanation can be given for the unsuccessful attempts to prepare tertiary alcohols of barenes by the reaction of barenyl-lithium derivatives with barene ketones[42,43]:



For the same reason formation of tertiary alcohols is not observed when lithiumbarenes interact with acid chlorides, the reaction halting at the ketone stage. This has been utilised by Zakharkin and L'vov[42,44] to prepare a large number of ketones of the barene series:

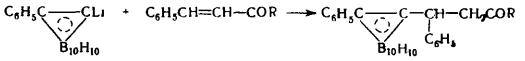


Dilithiumbarene reacts with carbonyl chloride to yield a cyclic diketone[45]:



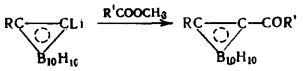
This compound, however, does not react with 1,1-dimethylhydrazine (which would be characteristic of the carbonyl group), owing to the influence of the barenyl cage.

Phenylbarenyl-lithium reacts smoothly with chalcone and with styryl t-butyl ketone in benzene solution to give the corresponding γ-ketones[46]:

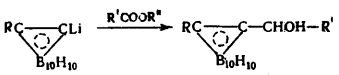


where R = C_6H_5, $C(CH_3)_3$.

Esters react with lithium derivatives of barene to form ketones or secondary alcohols, depending on the structure of the ester. Ketones are formed from the methyl esters of aromatic acids and the methyl and ethyl esters of aliphatic acids, whereas alcohols are the main products from ethyl, propyl, and isopropyl esters of aromatic acids[47]:

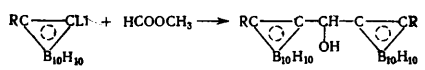


where R = C_6H_5 and R′ = C_6H_5, p-$CH_3C_6H_5$, p-BrC_6H_4; R = CH_3 and R′ = C_6H_5;



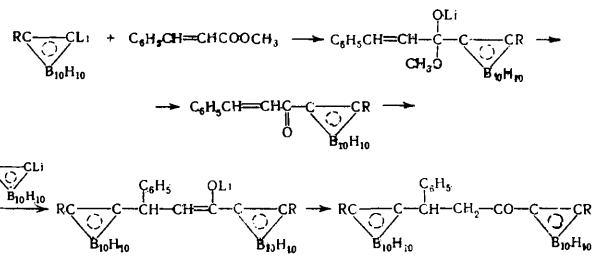
where R = R′ = C_6H_5 and R″ = C_2H_5, C_3H_7; R = CH_3, R′ = C_6H_5, and R″ = C_2H_5.

Lithiumbarenes react with methyl and ethyl formate similarly to Grignard reagents, yielding secondary alcohols containing two barene cages[48]:



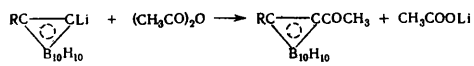
where R = CH_3, C_6H_5.

The reaction between lithium derivatives of barenes and methyl cinnamate takes place in two stages, involving the initial 1,2-addition of the lithiumbarene at the ester carbonyl group to form an $\alpha\beta$-unsaturated barenyl ketone, followed by 1,4-addition of a second lithiumbarene molecule[46]:

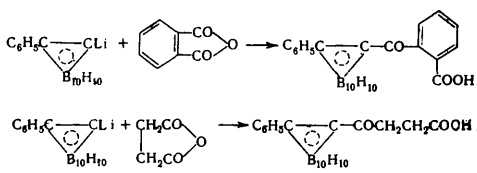


where R = CH_3, C_6H_5.

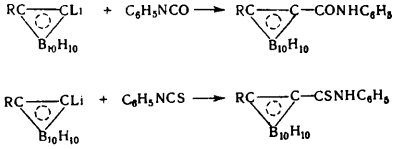
In contrast to the reactions of the usual organolithium compounds, the action of lithiumbarenes on carboxylic anhydrides yields barenyl ketones without the formation of tertiary alcohols[48,49]:



where R = CH_3, C_6H_5. With the anhydrides of dicarboxylic acids lithiumbarenes yield keto-acids of the barene series[48,49]:

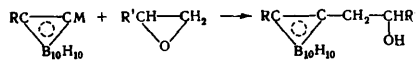


Lithium derivatives of barenes[48] and neobarenes[49] react smoothly with phenyl isocyanate and phenyl isothiocyanate to form the corresponding anilides of the barene- and neobarene-carboxylic and -carbothioic acids:



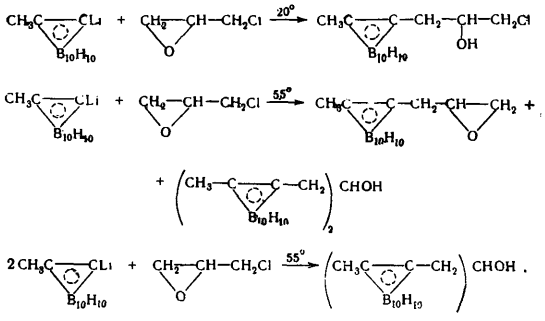
where R = CH_3, C_6H_5.

Lithiumbarenes in ether[16,17] and sodium barenes in liquid ammonia[20,21] react smoothly with α-epoxides to produce high yields of primary and secondary alcohols in which the hydroxyl is in the β-position relative to a carbon atom of the barene cage (the best results are obtained by conducting the reaction with the lithium derivatives in ether)[50]:

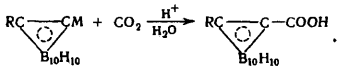


where R = H, CH_3, CH_2:CH, C_6H_5, R′ = H, CH_3, C_6H_5, and

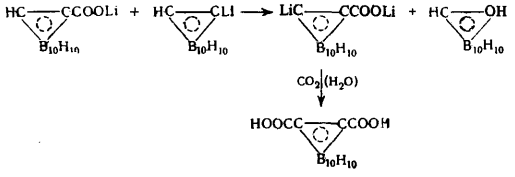
M = Li, Na. In the case of epichlorohydrin in the cold, the oxiran ring is opened without the chlorine atom being affected; when the temperature is raised a mixture of products is formed[50]:



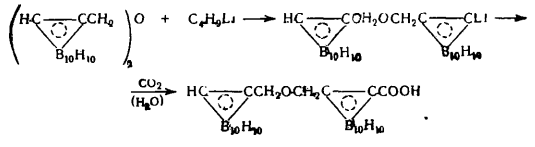
As has already been mentioned (p. 174) magnesium[22,25], lithium[12,15-17], and sodium[19] derivatives of barenes are important starting materials for the preparation of barenecarboxylic acids which are often difficultly accessible:



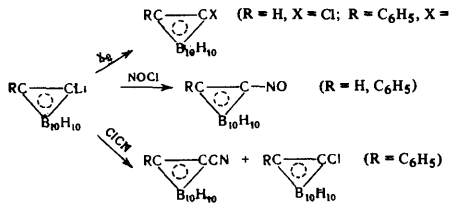
An interesting reaction was observed by Heying et al.[16], who, in attempting to prepare barenecarboxylic acid by treating barene with an equivalent quantity of butyl-lithium and then carboxylating the product, obtained a good yield of barenedicarboxylic acid, as a consequence of the exchange reaction



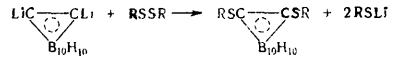
occurring at the instant of carboxylation. These workers explain the enhanced mobility of the hydrogen atom as a proton in lithium barenecarboxylate by the influence of the carboxy-group. Such a phenomenon is not observed in the absence of a carboxyl or when it is remote from the barene cage. Reaction between bisbarenylmethyl ether and an equivalent quantity of butyl-lithium followed by carboxylation yields only the monocarboxylic acid[51]:



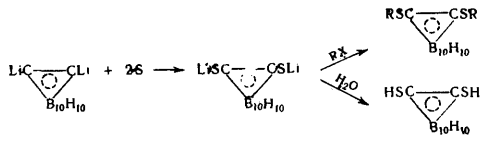
Barenyl-lithium derivatives have been used also for the preparation of halogenobarenes[17,35,44,52], nitrosobarenes[53,54], and cyanobarenes[55]:



Smith et al.[56], starting from dilithiumbarene and neobarene, obtained compounds containing a barene carbon–sulphur bond:

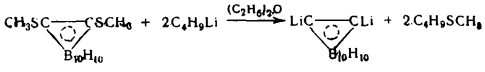


where R = CH_3, C_2H_5, $C_6H_5CH_2$, C_6H_5, $CH_3C_6H_4$;

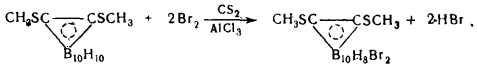


where R = H and X = Cl; R = CH_3 and X = I. Mono-, di-, and tri-*B*-bromobarenes also undergo these reactions. Sulphur dichloride reacts with dilithiumbarene to give polymeric substances of low molecular weight, containing a dithio-bond.

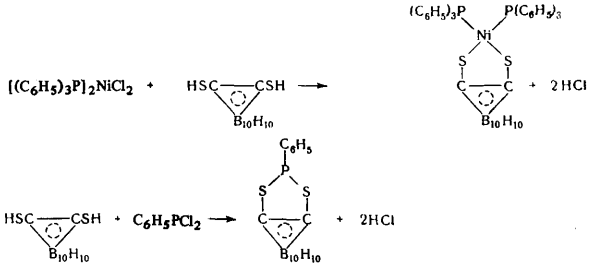
The barene carbon–sulphur bond is cleaved by the action of butyl-lithium. In contrast to dialkyl or mixed alkyl aryl sulphides, this involves nucleophilic attack at the sulphur atom with formation of a carbon–lithium bond[56]:



The electron-acceptor effect of the barene cage on the sulphur atom is shown also in the inability of barenyl sulphides to form sulphonium salts on treatment with bromine in boiling carbon tetrachloride or in carbon disulphide. The addition of aluminium chloride in the latter case merely leads to bromination of the barene cage:

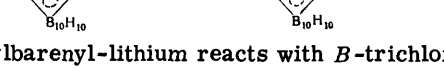


Barenedithiol reacts readily with dichlorobistriphenylphosphinenickel and phenylphosphonous dichloride to form the corresponding five-membered cyclic compounds[56]:

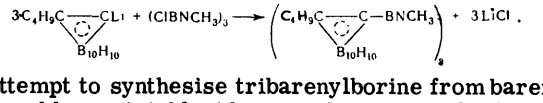


III. BARENYL DERIVATIVES OF BORON

A compound containing a barene carbon–boron bond was first obtained by the action of chlorobisdimethylaminoborine on barenyl-lithium[57]:



n-Butylbarenyl-lithium reacts with *B*-trichloro-*N*-trimethylborazole to give the corresponding barenyl derivative of borazole[57]:

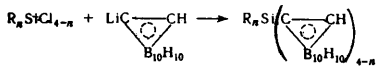


At attempt to synthesise tribarenylborine from barenyllithium and boron trichloride proved unsuccessful[57].

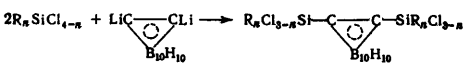
IV. DERIVATIVES OF GROUP IV ELEMENTS

1. Silicon

The specific features of barene compounds permitted the hope that organosilicon polymers containing barenyl radicals would possess unusual properties. This stimulated Papetti, Heying, and their coworkers [58-60] to examine the properties of diverse compounds containing a (barene) carbon–silicon bond, which they synthesised by the action of dilithiumbarenes on various organic and inorganic silicon derivatives containing a silicon–chlorine bond:

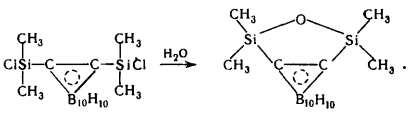


where $n = 2$ and R = CH_3; $n = 3$ and R = CH_3, C_6H_5;

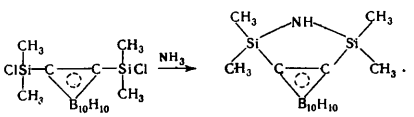


where $n = 0$, 1 and R = CH_3; $n = 2$ and R = CH_3, C_6H_5.

An attempt was made [58] to convert the resulting bis-chlorodimethylsilylbarene into the corresponding silanol, which was necessary for synthesising a polyorganosiloxane. However, this attempt was unsuccessful, owing to the tendency of the diols to undergo cyclisation with formation of a five-membered siloxane ring containing the two carbon atoms of the barene:

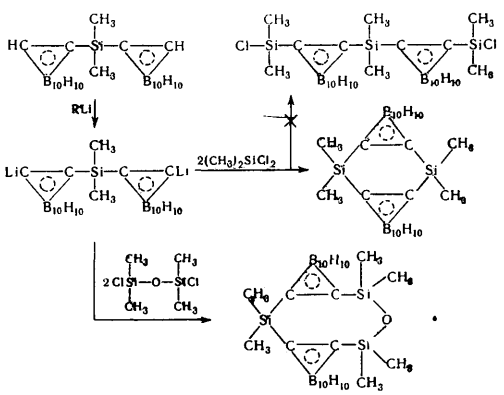


An analogous cyclisation has been observed in the action of ammonia [58]:

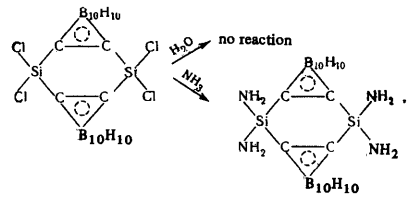


Several workers [16,17,61] have obtained similar compounds containing a ring comprising the two barene carbon atoms together with C–C–C and C–O–C groupings. This ease of formation of five-membered rings is probably due to structural peculiarities in barene (the carbon–carbon distance and the bond angles at a carbon atom).

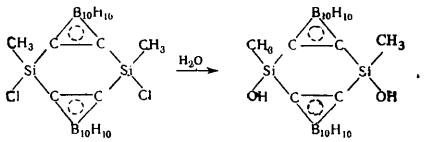
Failure attended also an attempt to obtain an acyclic compound by the action of even excess of dimethyldichlorosilane and tetramethyldichlorosiloxane on the dilithium derivative of dibarenyldimethylsilane [59]:



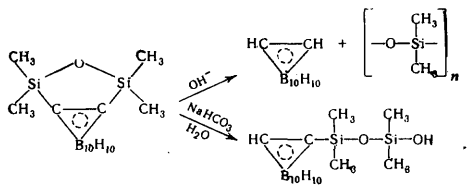
The properties of silicon derivatives of barene are greatly affected also by the strong electron-acceptor action of the barenyl group, as is shown in particular in the stability to hydrolysis of the silicon–chlorine bond in the cyclic tetrachloro-1,4-disilin formed by two barenylidene groups. However ammonia reacts quantitatively with this compound [59]:



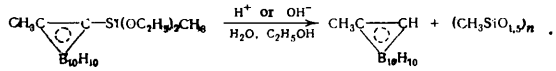
Replacement of one chlorine atom at each silicon atom by a methyl group produces a sharp increase in the ability of the silicon–chlorine bond to be hydrolysed by water, this probably being due to an increase in the ionic character of the bond:



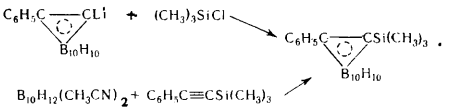
The electron-acceptor influence of the barene cage can explain also the tendency of barenylsilanes to cleavage of the silicon–carbon (barene) bond in the presence of bases [59]:



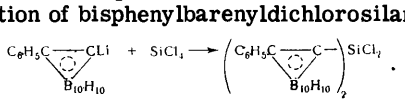
Observations by American chemists [62] indicate that both acids and bases cause rupture of the silicon–carbon bond:



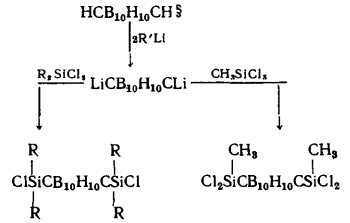
The synthesis of barenylsilanes has been accomplished also by Zakharkin et al. [63] in the case of 1-phenyl-2-trimethylsilylbarene. These workers showed that it was in principle possible to obtain this compound from decaborane–bisacetonitrile and 1-phenyl-2-trimethylsilylacetylene [63]:



Reaction between silicon tetrachloride and phenylbarenyl-lithium (2–4 moles per mole of the halide) results only in the formation of bisphenylbarenyldichlorosilane [64]:

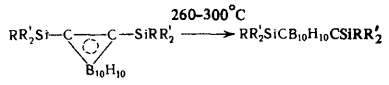


Neobarenylsilanes were obtained [60] in the same way as barenylsilanes:



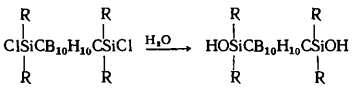
§ Here and subsequently the formula $HCB_{10}H_{10}CH$ will denote neobarene.

where R = CH_3, C_6H_5. It was also noticed[65] that barenylsilanes were able to isomerise into neobarenylsilanes at 260–300°C (barene itself isomerises into neobarene at 500°C [12]):

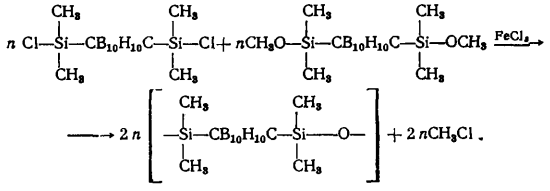


where R = CH_3 and R′ = CH_3, C_6H_5; R = Cl and R′ = C_6H_5; and R = C_6H_5 and R′ = CH_3.

Since the carbon atoms in neobarenes are remote from one another, dihydroxy-derivatives of neobarenylsilanes, unlike their barene analogues, exhibit no tendency to cyclisation[60]:



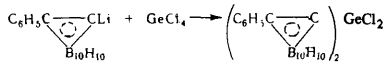
where R = CH_3, C_6H_5. This has enabled neobarenylsilanes to be used in the synthesis of silicon polymers containing the group $-CB_{10}H_{10}C-$ in the polymer chain. However, such polymers could not be synthesised by the hydrolysis of bisdimethylchlorosilylneobarene. The use of various conditions of hydrolysis produced only stable diols[66]. The first polymer of this type was obtained by Papetti et al.[66] by copolymerisation of bisdimethylchlorosilylneobarene with bismethoxydimethylsilylneobarene in the presence of catalytic quantities of iron(III) chloride:



The resulting polysiloxane was a white crystalline substance of molecular weight 16 000. Several polymers containing various combinations of neobarenylene groups and siloxane residues were obtained in the same way.

2. Germanium

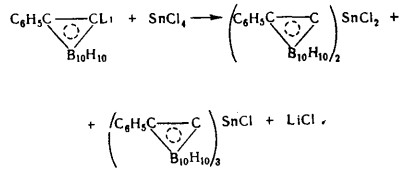
The only barenyl derivative of germanium yet known was obtained by the interaction of phenylbarenyl-lithium and germanium tetrachloride[64]:



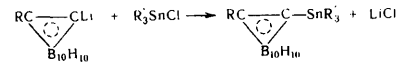
As in the reaction with silicon tetrachloride (see preceding subsection), not more than two chlorine atoms could be replaced owing to steric hindrance due to the bulky barene cage.

3. Tin

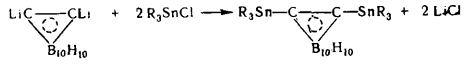
The increase in atomic radius on passing from silicon and germanium to tin makes it possible to obtain a derivative in which tin is attached to three barenyl groups. Thus the reaction between phenylbarenyl-lithium and tin tetrachloride results in a mixture of the corresponding chloride and dichloride[64]:



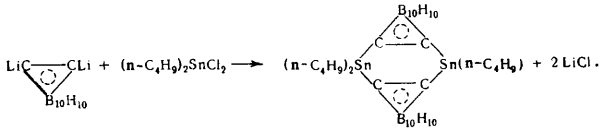
In the absence of steric hindrance, organotin halides are readily alkylated by lithiumbarenes[63,64]:



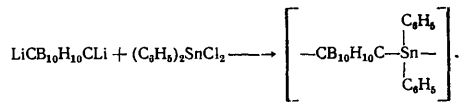
where R = H, C_6H_5, and R′ = n-C_3H_7, C_6H_5. Dilithiumbarene reacts with tri- and di-alkyltin chlorides to give compounds containing two tin atoms in the molecule[64,67]:



where R = n-C_3H_7, C_6H_5; and

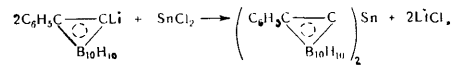


Replacement of dilithiumbarene by dilithiumneobarene in the reaction with dialkyltin dichlorides leads to the formation of—instead of cyclic compounds—polymeric products[68] having molecular weights up to 5750:



A study of the Mössbauer spectra of the organotin compounds obtained has shown[67] that the barenyl group exerts a greater electron-acceptor action on the tin atom than any organic substituent hitherto examined by this method. In its effect on the electronic environment of the tin nucleus it is comparable only with the pentafluorophenyl group. It can be concluded from the Mössbauer spectra that the ionic character of the tin–chlorine and tin–carbon (barene) bonds in trisphenylbarenyltin chloride and bisphenylbarenyltin dichloride is similar to, while the symmetry of the electric field at the tin nucleus is considerably greater than that in the analogous phenyl derivatives, as a consequence of the strong electron-acceptor influence of the barenyl group.

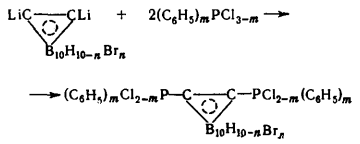
Interaction between phenylbarenyl-lithium and anhydrous tin(II) chloride yields bisphenylbarenyltin, the first derivative of bivalent tin, stable in an inert atmosphere, and showing no tendency to polymerise[67]:



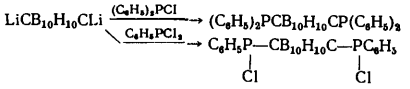
V. DERIVATIVES OF GROUP V ELEMENTS (PHOSPHORUS, ARSENIC, ANTIMONY)

Mixed barenyl(phenyl)phosphines have been obtained by the reaction of phenylchlorophosphines with the dilithium

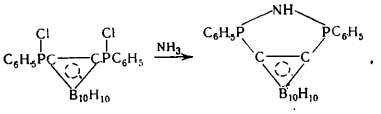
derivatives of barene[69,70], neobarene[71], and *B*-polyhalogenobarenes[30]:



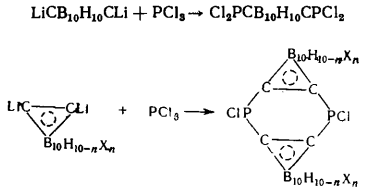
where $n = 0$ and $m = 1, 2$; $n = 1-3$ and $m = 2$; and $n = 2$ and $m = 1$; also



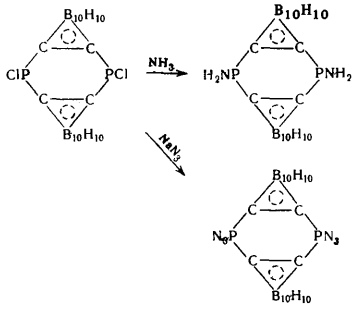
The action of ammonia on *PP'*-dichloro-*PP'*-diphenylbarenylenediphosphine yields a five-membered ring typical of the chemistry of the barenes[69]:



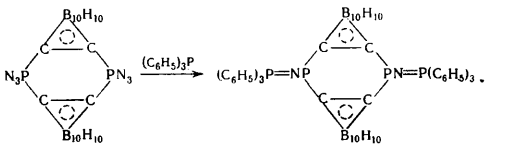
With phosphorus trichloride dilithiumneobarene gives *P*-tetrachloroneobarenylenediphosphine[71], whereas dilithiumbarene gives a six-membered ring containing two phosphorus atoms[30,69,70]:



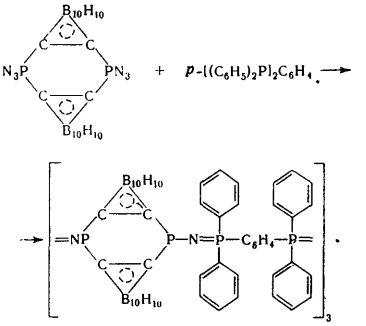
where X = Br, Cl and $n = 0-4$. The chlorine atoms in the resulting compound are readily replaced by the action of ammonia and of sodium azide[69]:



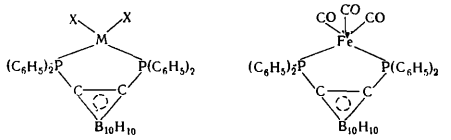
The resulting azido-derivative undergoes two very interesting reactions, the first of which yields a stable phosphine imide derivative[69]:



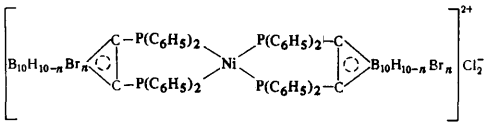
The second reaction[69] gives an oligomer of molecular weight ~ 2500, which has been used as a bonding agent in the manufacture of asbestos materials stable at high temperatures[72]:



Smith[73], and also Zakharkin and Zhigareva[74], discovered that *PP'*-tetraphenylbarenylenediphosphine was able to form stable five-membered chelate complexes with transition metals:

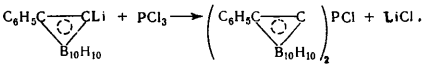


where M = Ni and X = CO, Cl; M = Pd and X = Cl; and also

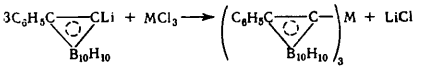


in which $n = 0-3$.

As with barenyl derivatives of Group IV elements, steric hindrance due to the bulky barenyl group is shown in the impossibility of substituting all three chlorine atoms when phenylbarenyl-lithium is treated with phosphorus trichloride[64]:



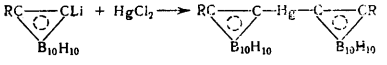
However, the increase in atomic radius on passing to arsenic and antimony compensates for the steric factors, and the halides of these two elements readily form trisubstituted derivatives[64]:



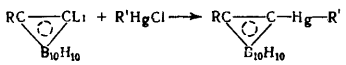
where M = As, Sb.

VI. MERCURY DERIVATIVES

In view of the part played by organomercury compounds in the study of the properties of the metal–carbon bond, the organomercury derivatives of barenes are of great value for an understanding of the peculiarities in the chemical behaviour of the metal–barene carbon bond. They were first obtained by Zakharkin and his coworkers[63,64,75,76] by the action of *C*-lithium derivatives of barenes on mercury(II) chloride or an alkylmercury halide:



where R = H, CH_3, $CH_2:CH$, C_6H_5; or

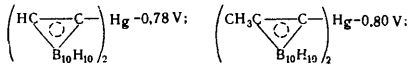


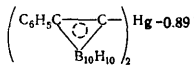
where R = H, CH_3, $CH_2:CH$, C_6H_5 and R′ = CH_3; R = C_6H_5 and R′ = C_6H_5, ferrocenyl.

Symmetrical barenylmercury compounds are distinguished by great stability, remaining unchanged even on prolonged heating at 300–350°C. The unsymmetrical compounds RHgR′ (in which R and R′ are barenyl radicals) do not tend to disproportionate into R_2Hg and R'_2Hg even in the melt (150–200°C) [75].

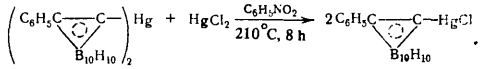
During the action of phenylbarenyl-lithium on mercury(II) chloride the reaction mixture contains no phenylbarenylmercury chloride, which is an unusual feature in the chemistry of organomercury compounds. Bisphenylbarenylmercury is immediately formed, while the excess of mercuric chloride does not react. An analogous phenomenon is observed with vinyl- and methyl-barenyl-lithium. Thus the alkylbarenylmercury chloride is very readily alkylated in comparison with the initial mercury chloride, and this has no analogy in organomercury chemistry.

The strong electron-acceptor effect of the barenyl group towards the mercury atom is confirmed by an examination of barenylmercury compounds by polarographic reduction. Some half-wave potentials obtained (in dimethylformamide) are indicated below [76]



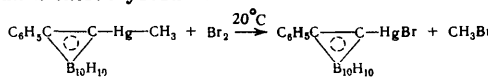


With the mercury derivatives of barenes, especially the symmetrical compounds, cleavage of the carbon–mercury bond under the influence of electrophilic reagents [hydrogen chloride, bromine, mercury(II) chloride], which is so common in the chemistry of ordinary organomercury compounds, goes either with difficulty or not at all. Thus phenylbarenylmercury chloride is not formed by the prolonged boiling of bisphenylbarenylmercury with mercury(II) chloride in alcohol. It was successfully obtained only when the reactants were heated in boiling nitrobenzene (for 8 h) [75,76]:

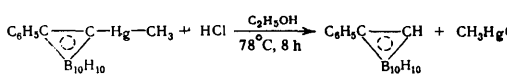


The mercury–carbon bond in symmetrical barenylmercury compounds is not ruptured by the action of bromine in boiling dichloromethane and benzene or on boiling with alcoholic hydrogen chloride solution (for 20 h).

When bromine acts on methyl(phenylbarenyl)mercury in the cold, it is only the mercury–methyl bond which is broken. The mercury–carbon (barene) bond remains unchanged, phenylbarenylmercury bromide being formed in almost quantitative yield [76]:

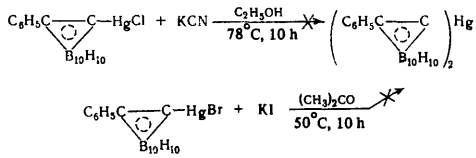


However, the action of alcoholic hydrogen chloride on methyl(phenylbarenyl)mercury produces rupture of the mercury–carbon (barene) bond with formation of phenylbarene [63]:



The above results indicate that cleavage of the mercury–carbon bond proceeds by different mechanisms under the influence of bromine and of proton acids.

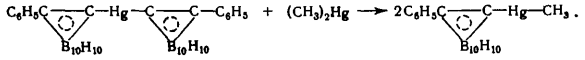
Phenylbarenylmercury chloride and bromide were found to be stable to the action of such strong symmetrising agents as potassium cyanide and iodide [76]:



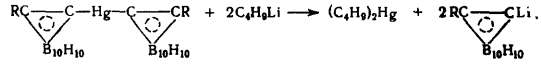
One reason for the anomalous behaviour of barenylmercury compounds in reactions involving electrophilic substitution at a barene carbon atom is probably the unusual valency state of the six-coordinated barene carbon atom, which is unable to form a cyclic transition state, as this would require the unlikely and unprecedented increase in the coordination number of carbon to seven. Furthermore, formation of such a transition complex is prevented also by steric hindrance due to the icosahedral barene cage. It must also be reckoned that the barene cage will exert a strong electron-acceptor influence, preventing localisation of a negative charge on a barene carbon atom.

Nothing that has been stated above excludes the possibility, however, of a unimolecular reaction (S_E1), which probably occurs if reaction with the electrophilic reagent does take place [reaction with mercury(II) chloride in boiling nitrobenzene, protolysis].

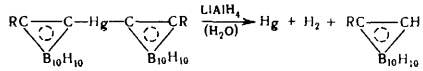
Under severe conditions (230°C for 9 h) even dimethylmercury reacts with bisphenylbarenylmercury, yielding methyl(phenylbarenyl)mercury [77]:



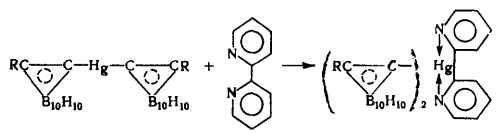
Cleavage of the mercury–carbon (barene) bond occurs far more readily during nucleophilic attack at the mercury atom. Thus symmetrical barenyl derivatives of mercury react with such nucleophilic reagents as butyl-lithium even in the cold, with the formation of products of the exhaustive exchange of radicals [77]:



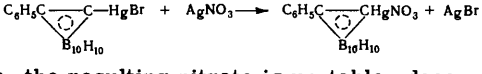
Bismethylbarenyl- and bisphenylbarenyl-mercury are easily reduced by lithium tetrahydroaluminate [77]:



The coordinative unsaturation of a mercury atom attached to two barenyl radicals is so great that even symmetrical barenylmercury compounds readily form complexes with 2,2′-bipyridyl [77]:



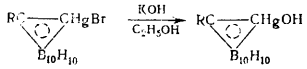
The halogen in barenylmercury halides is replaced by the action of an aqueous–alcoholic solution of silver nitrate [77]:



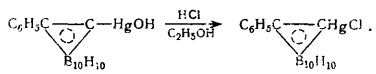
However, the resulting nitrate is unstable, decomposing

even at room temperature with the evolution of oxides of nitrogen.

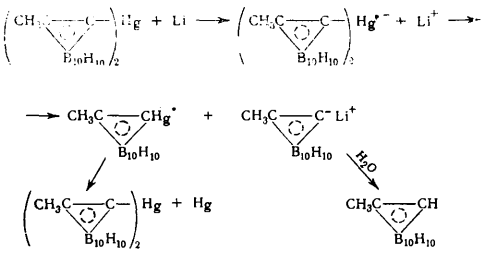
Alcoholic alkali acts on barenylmercury bromides, the bromine being easily replaced by hydroxyl[77]:



where R = CH_3, C_6H_5. The resulting hydroxides are difficultly identifiable substances which are unstable in air. Phenylbarenylmercury hydroxide reacts with hydrochloric acid to give phenylbarenylmercury chloride:

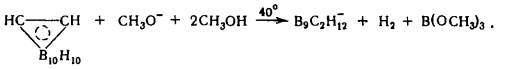


Symmetrical barenyl derivatives of mercury, which are stable towards metals (lithium, aluminium) when heated in an inert medium (xylene), react with lithium in dimethoxyethane even in the cold, as has been shown with bismethylbarenylmercury[77]. The rate of the process is probably determined by electron transfer from the metal to a molecule of the organomercury compound:

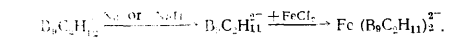


VII. ORGANOMETALLIC DERIVATIVES OF DICARBAUNDECABORANE

Treatment of barene with alcoholic alkali results in its partial cleavage with the formation of an anion of dicarbaundecaborane[78]:



By using this anion, Hawthorne and his coworkers were able to synthesise a series of "sandwich" derivatives, which are analogues of the cyclopentadienyl compounds of transition metals (iron, manganese, rhenium, cobalt). The first member of this series was obtained[79] by reaction between iron(II) chloride and the doubly charged anion $B_9C_2H_{11}^{2-}$, formed from $B_9C_2H_{12}^-$ by the action of metallic sodium or of sodium hydride:



Oxidation of the dianion $Fe(B_9C_2H_{11})_2^{2-}$ in the air yields the analogue of the ferricinium cation $Fe(B_9C_2H_{11})_2^-$. Salts of this anion are stable towards acids and bases, and remain unchanged when heated to 300°C.

When a mixture of cyclopentadienylsodium and the disodium salt of the anion $B_9C_2H_{11}^{2-}$ in tetrahydrofuran is boiled with iron(II) chloride, the corresponding mixed derivative π-$C_5H_5Fe(\pi$-$B_9C_2H_{11})^-$ is formed[80]. Study of the crystal structure of this compound showed[81] that the iron atom is approximately at the same distance from the five carbon atoms of the cyclopentadienyl ring (2.07 Å) as from the two carbon atoms (2.04 Å) and the three boron atoms (2.09 Å) of the dicarbaundecaborane. This and several other investigations[79,80,82] have enabled the structure of the above compounds to be established (Fig. 2).

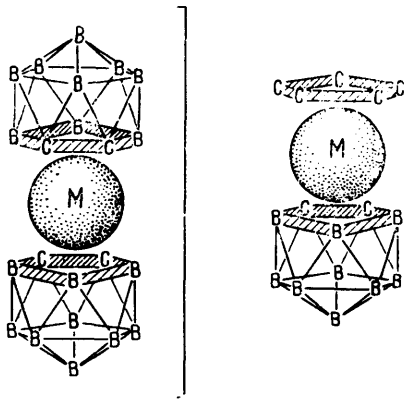


Figure 2. Structure of "sandwich" derivatives of the dicarbaundecaborane anion.

Sandwich derivatives of other metals have also been prepared[83-86]—$(B_9C_2H_{11})Mn(CO)_3^-$, $(B_9C_2H_{11})Re(CO)_3^-$, $(B_9C_2H_{11})_2Co^-$, $(C_5H_5)Co(B_9C_2H_{11})$, and $[\pi$-$(C_6H_5)C_4]Pd$.$[\pi$-$B_9C_2H_{11}]$.

Thus the organoelementary chemistry of these novel non-coplanar aromatic compounds—the barenes—has accumulated within a short time considerable and interesting information. Work on these lines is being vigorously prosecuted.

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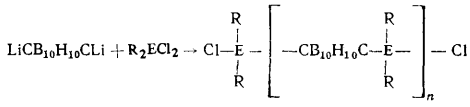
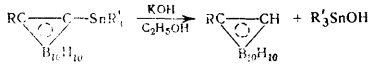
Several interesting researches have recently been done on the barenyl derivatives of Group IV elements. Thus some American chemists[89] have prepared germanium and tin polymers containing a neobarene grouping in the main chain, and having molecular weights up to 9000:

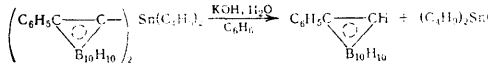


where E = Ge, Sn and R = CH_3, C_6H_5.

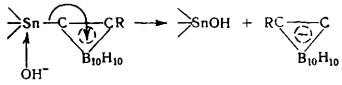
Bregadze and Okhlobystin have shown[90] that the tin–carbon bond in barenyl derivatives of tin is easily cleaved by aqueous and alcoholic solutions of alkalis, with formation of the corresponding barenes and organotin hydroxides:



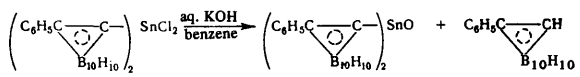
where R = C_6H_5, H and R′ = C_3H_7, C_6H_5; also



The rupture of tin–carbon bonds probably occurs by direct nucleophilic attack on the tin atom, with as a consequence heterolytic dissociation and formation of a barenyl anion:



The lability of the tin–carbon (barene) bond under nucleophilic attack is so great that, when a benzene solution of bisphenylbarenyltin dichloride is treated with aqueous alkali, there is competitive cleavage of tin–carbon and tin–chlorine bonds:



The tin–carbon bonds in the dichloride undergo cleavage even during chromatography on aluminium oxide, which results in the formation of phenylbarene.

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The Chemistry of Manganese Carbonyl

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CONTENTS

I. Introduction 185
II. Structure of manganese carbonyl 185
III. Methods of preparation and properties 185
IV. Hydrogen carbonylmanganates and allied compounds 186
1. Preparation and properties of hydrogen carbonylmanganates 186
2. Ionic complexes of manganese carbonyl 186
3. Polymetallic derivatives 186
V. Derivatives of manganese carbonyl containing a carbon–manganese σ-bond 187
1. Alkyl- and acyl-manganese pentacarbonyls 187
2. Perfluoro-derivatives 188
VI. Halogeno-carbonyls and allied compounds 189
1. Halogeno-derivatives of manganese carbonyl 189
2. Nitrato- and thiocyanato-compounds 189
VII. Products resulting from substitution of carbonyl groups 189
1. Isocyanide and nitrile complexes 189
2. Nitrosyl derivatives of manganese carbonyl 190
3. Substitution of carbonyl groups by nitrogen compounds 190
4. Phosphorus, arsenic, and antimony derivatives 190
5. Compounds containing sulphur and tellurium 191
VIII. π-Hydrocarbon manganese carbonyl derivatives 192
IX. Compounds containing a boron atom 194
X. Applications of manganese carbonyl derivatives 194

I. INTRODUCTION

There is now a vast review literature on the chemistry of the carbonyls of chromium, molybdenum, tungsten, iron, cobalt, and nickel[1-4]. However, although more than two hundred papers and patents have been published since 1954 on the chemistry of manganese carbonyl, no review of this subject has appeared. Our paper represents an attempt to fill this gap.

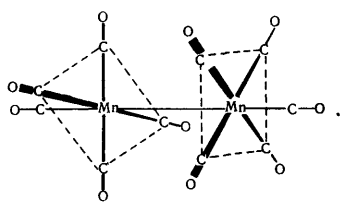
Manganese carbonyl and its derivatives possess several interesting properties, so that they attract wide attention from research workers in various specialised fields.

The present review deals with the structural peculiarities, methods of preparation, chemical properties, and chief fields of practical application of manganese carbonyl and its derivatives other than π-cyclopentadienylmanganese tricarbonyl, the chemistry of which will be discussed in a special paper. The literature published up to the beginning of 1966 is covered in the review.

II. STRUCTURE OF MANGANESE CARBONYL

Decacarbonyldimanganese $Mn_2(CO)_{10}$, like other carbonyls of transition metals, conforms to Sidgwick's rule, according to which the manganese atom must acquire a further eleven electrons. By interacting with five molecules of carbon monoxide the manganese atom gains ten electrons. The electron shell is completed by the formation of a bond between two atoms of the metal.

The decacarbonyldimanganese molecule can be represented by two octahedral groups, the centre of each being occupied by a manganese atom, while five corners are occupied by carbonyl groups, and the sixth by the adjacent metal atom:



A bond is formed between the manganese atom and a carbonyl group by coordination of the free d^2sp^3 orbitals of the manganese atom with the $(s-p_x)^2$ electrons of the carbon atom. It follows from the principle of maximum overlap of atomic orbitals that all the Mn–C–O groups are linear[5-7]. This should not involve any considerable change in the distribution of the electron cloud between the carbon and oxygen atoms, so that, as in free carbon monoxide, the carbon–oxygen bond should be somewhat in the nature of a triple bond. It has in fact been found that the carbon–oxygen distance in the $Mn_2(CO)_{10}$ molecule is 1.16 Å, which is intermediate between the values of 1.128 Å for the triple bond C≡O in carbon monoxide and 1.225 Å for the double bond C=O in formaldehyde.

Electrical neutrality of the manganese atom is probably established by some displacement of its d-electrons towards the carbon atom, as a result of which the manganese–carbon bond is partly double-bonded in character. It has been found experimentally[9] that the length of the manganese–carbon bond is ~ 1.83 Å, which is considerably less than the sum of the covalent radii.

The character of the manganese–manganese bond has not yet been elucidated. Its length in the $Mn_2(CO)_{10}$ molecule is 2.93 Å, whereas the sum of the covalent radii should be only 2.74 Å. The anomalous character of the manganese–manganese bond is confirmed also by the relatively low bond energy of 34 ± 13 kcal mole^{-1}.[10]

It has been found[12-14] that the axial carbonyl group is somewhat more firmly bound to the manganese atom than are the equatorial groups, although the difference in bond energy is not large. This can probably be explained by a breakdown in the symmetry of the electron cloud owing to the presence of different substituents around the manganese atom.

The structure given for the manganese carbonyl molecule agrees well with X-ray data[8].

III. METHODS OF PREPARATION AND PROPERTIES

In contrast to the carbonyls of nickel, chromium, and iron, decacarbonyldimanganese is not formed by the direct interaction of powdered metallic manganese and carbon monoxide. All the methods at present known for its preparation involve reducing a salt or an oxide of manganese to the metal and reaction of the latter *in situ* with carbon monoxide[15].

The existence of a manganese carbonyl was first reported in 1949 by Hurd et al.[16], who obtained mass-spectrometric evidence of its formation during the reduction of manganese iodide by a Grignard reagent in the presence of carbon monoxide. In 1954 Brimm et al.[17,18] obtained a 1% yield of decacarbonyldimanganese by the reaction

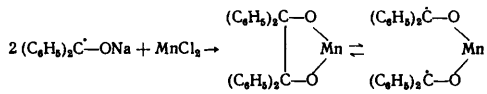
$$2\,MnI_2 + 2\,Mg + 10\,CO \rightarrow Mn_2(CO)_{10} + 2\,MgI_2.$$

The method of preparing manganese carbonyl by means of Grignard reagents has since been considerably improved[19-23].

Metallic sodium[24], sodium hydride, and lithium tetrahydroaluminate[25,26] can be employed as reducing agents. In the last case hydrogen pentacarbonylmanganate is formed, and this then decomposes with the evolution of hydrogen:

$$2\,HMn(CO)_5 \rightarrow Mn_2(CO)_{10} + H_2.$$

It is of interest to obtain manganese carbonyl by means of certain radical-anions, e.g. benzophenone ketyl[27,28]. The manganese salt resulting from the double decomposition



readily decomposes on heating, with the separation of metallic manganese:

$$[(C_6H_5)_2\dot{C}{-}O]_2Mn \rightarrow 2\,(C_6H_5)_2C{=}O + Mn.$$

This reacts with carbon monoxide under pressure, to form manganese carbonyl:

$$2\,Mn + 10\,CO \rightarrow Mn_2(CO)_{10}.$$

A disadvantage of this method is the difficulty of separating the manganese carbonyl from benzophenone. Other radical-anions, e.g. naphthalene–sodium[29], can be used instead of ketyls.

The best yields (up to 54%) of decacarbonyldimanganese are obtained by using as reductants diethylzinc[30], a trialkylaluminium[31,32], or metallic aluminium activated by an organoaluminium compound[33].

Finally, decacarbonyldimanganese can be prepared from derivatives of cyclopentadienylmanganese tricarbonyl by the action of metallic sodium in the presence of diglyme[34,35] or an amine[36].

Decacarbonyldimanganese consists of golden-yellow crystals melting at 154–155°C. It readily sublimes in a vacuum, the heat of sublimation being 15 kcal mole^{-1}.[37] In the air at room temperature it is stable for several months. When heated in air above 110°C it decomposes with the formation of a metallic mirror and carbon monoxide. In an atmosphere of carbon monoxide it is stable up to 250°C.

Manganese carbonyl is soluble in most organic solvents, but is insoluble in water. In air the solutions decompose rapidly at room temperature.

The infrared absorption spectrum of decacarbonyldimanganese is characterised by strong bands at 2063, 2028, and 1997 cm^{-1} which are assigned to the carbonyl groups, and two bands in the region of 640 cm^{-1} attributable to the manganese–carbon bond[11,37]. For the nuclear magnetic resonance (n.m.r.) spectra of manganese carbonyl see Ref. 38.

IV. HYDROGEN CARBONYLMANGANATES AND ALLIED COMPOUNDS

1. Preparation and Properties of Hydrogen Carbonylmanganates

Two hydrogen carbonylmanganates—$HMn(CO)_5$ and $H_2Mn_2(CO)_9$—are formed by the reduction of decacarbonyldimanganese with hydrogen, lithium, tetrahydroaluminate[39], or a hydroborate[40] in an inert solvent. Metals (magnesium, aluminium, amalgams) and other reducing agents can also be used[41].

Hydrogen pentacarbonylmanganate $HMn(CO)_5$ is a colourless liquid (m.p. = −24.6°C, $d^{20} = 1.465$, $n_D^{20} = 1.518$, and dipole moment = 0.70 D), which decomposes at 100°C.[42,43] The infrared absorption spectra of this compound and its deuterio-analogue are characterised by carbonyl bands in the range 2150–1950 cm^{-1}, bands at 1782, 735, 664, 615, and 458 cm^{-1} assigned to the hydrogen–manganese bond, and bands at 1287 and 676 cm^{-1} ascribed to the manganese–deuterium bond[11,44–46].

The $HMn(CO)_5$ molecule has the shape of a distorted octahedron, the length of the hydrogen–manganese bond being 1.5–1.6 Å.[47,48]

The second hydrogen carbonylmanganate $H_2Mn_2(CO)_9$ is unknown in the pure form, but several of its derivatives have been obtained.

Hydrogen carbonylmanganates are weak acids, the dissociation constant of $HMn(CO)_5$ being 0.8×10^{-7}. In aqueous alkalis the hydrogen atom is replaced by an alkali-metal cation[49]:

$$HMn(CO)_5 + KOH \rightarrow KMn(CO)_5 + H_2O.$$

The same salts can be obtained by reducing decacarbonyldimanganese with the alkali metals or their amalgams[50,51].

Hydrogen carbonylmanganates react with Lewis bases to form saltlike complexes[40]. With pyridine, for example, the reaction is

$$6\,HMn(CO)_5 + 12\,C_5H_5N \rightarrow 2\,[Mn(C_5H_5N)_6][Mn(CO)_5]_2 + 10\,CO + 3H_2.$$

Hydrogen carbonylmanganates are strong reducing agents. According to Hieber and Wagner[42], the reduction potential of hydrogen pentacarbonylmanganate in aqueous alkali at 20°C is −0.68 V. In inert solvents this compound reduces halogens:

$$2\,HMn(CO)_5 + I_2 \rightarrow Mn_2(CO)_{10} + 2\,HI.$$

These hydrogen derivatives are able to react also with halogenated hydrocarbons. On ultraviolet irradiation in chloroform or carbon tetrachloride they are converted into the halogenocarbonylmanganese derivatives—$MnCl(CO)_5$ and $[MnCl(CO)_4]_2$.

Hydrogen pentacarbonylmanganate serves as starting material for the preparation of various organic derivatives of manganese carbonyl. With diazomethane, for example, it forms pentacarbonylmethylmanganese[52]:

$$HMn(CO)_5 + CH_2N_2 \rightarrow MnCH_3(CO)_5 + N_2.$$

Hydrogen pentacarbonylmanganate has found an interesting application in the preparation of fluoroalkyl derivatives of manganese carbonyl[43]:

$$HMn(CO)_5 + CF_2{=}CF_2 \rightarrow HCF_2{-}CF_2{-}Mn(CO)_5.$$

2. Ionic Complexes of Manganese Carbonyl

Besides the alkali-metal salts of the hydrogen carbonylmanganates, several compounds are known which are formed by the pentacarbonylmanganate ion with complex cations. In contrast to the analogous complexes of iron and cobalt, they can be obtained only in alkaline solution, owing to the acidic character of hydrogen pentacarbonylmanganate. Hieber and Schropp[53] isolated complex salts formed with the tri-*o*-phenanthroline-nickel(II) and -iron(II), dibenzenechromium(I), and dicyclopentadienylcobalt(I) cations. It is interesting that the dibenzenechromium salt is readily decomposed even at room temperature:

$$2\,[Cr(C_6H_6)_2][Mn(CO)_5] \rightarrow Mn_2^0(CO)_{10} + 2\,Cr^0(C_6H_6)_2$$

whereas the other complexes are considerably more stable. Salts of analogous structure are formed also by the interaction of decacarbonyldimanganese with pyridine[54] and with 1,10-phenanthroline[55].

Complexes are known also in which the carbonylmanganese group is the cation. Such compounds were first obtained by Fischer and his coworkers[56,57] by the reaction

$$ClMn(CO)_5 + AlCl_3 + CO \rightarrow [Mn(CO)_6]^+AlCl_4^-.$$

Instead of a carbon monoxide molecule, an ethylene molecule can be introduced into the cation:

$$ClMn(CO)_5 + AlCl_3 + C_2H_4 \rightarrow [Mn(CO)_5C_2H_4]^+AlCl_4^-.$$

Several complex salts have been obtained by the interaction of such carbonylmanganese cations with various anions[58–61]. All these compounds are usually stable in an inert atmosphere for several days, but they decompose rapidly in air in the presence of moisture.

3. Polymetallic Derivatives

Several compounds are known in which the manganese atom is attached by a covalent bond to atoms of other metals.

Hieber and Schropp[53] obtained mercury derivatives of manganese carbonyl:

$$2KMn(CO)_5 + Hg(CN)_2 \rightarrow [Mn(CO)_5]_2Hg + 2KCN.$$

The same compound was isolated by King[58] from the reaction between sodium pentacarbonylmanganate and sodium amalgam in the presence of 1,4-dibromobutane. Bis-pentacarbonylmanganesemercury readily reacts with mer-

cury halides to form complexes which are practically undissociated:

$$[Mn(CO)_5]_2Hg + HgCl_2 \rightarrow [Mn(CO)_5]_2Hg \cdot HgCl_2 \text{ or } (CO)_5MnHgCl.$$

In the reaction of potassium pentacarbonylmanganate with alkylmercury compounds, the mixed organomercury compounds which are probably formed as intermediates disproportionate with separation of the dialkylmercury:

$$RHgOH + KMn(CO)_5 \rightarrow [RHg—Mn(CO)_5] \rightarrow R_2Hg + [Mn(CO)_5]_2Hg.$$

This reaction may find application for the synthesis of fully organic mercury compounds.

Compounds containing a manganese–metal bond have been obtained by treating sodium pentacarbonylmanganate with chlorine derivatives of various metals[62]:

$$L_nMCl_m + m\,NaMn(CO)_5 \rightarrow L_nM[Mn(CO)_5]_m + m\,NaCl$$

where L = alkyl, aryl, aralkyl, alkaryl, or a radical containing phosphorus, arsenic, or antimony and M = Sn, Si, Ge, Ag, Au, Cu, etc.[64–67]

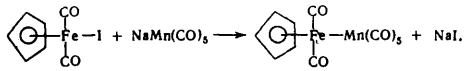
Trichlorogermanylmanganese pentacarbonyl was synthesised by a somewhat different method[63]:

$$Cl_3GeH + ClMn(CO)_5 \rightarrow Cl_3Ge—Mn(CO)_5 + HCl.$$

Stable bispentacarbonylmanganesegermane was prepared by Stone and his coworkers[64] by the reaction of hydrogen pentacarbonylmanganate with germane:

$$GeH_4 + 2HMn(CO)_5 \rightarrow H_2Ge[Mn(CO)_5]_2 + 2H_2.$$

The so called "mixed" carbonyls—i.e. compounds containing carbonyl groups of other metals as well as the pentacarbonylmanganese group—belong to this same type of compounds. The first such compound was cyclopentadienyldicarbonyliron–pentacarbonylmanganese, obtained in 40% yield by King et al.[78] by the reaction



Analogous methods were used to prepare "mixed" carbonyls of manganese and rhenium[79]:

$$(CO)_5ReCl + NaMn(CO)_5 \rightarrow (CO)_5Re—Mn(CO)_5 + NaCl$$

$$(CO)_5ReNa + ClMn(CO)_5 \rightarrow (CO)_5Re—Mn(CO)_5 + NaCl$$

as well as cobalt[80], molybdenum, and tungsten[81].

V. DERIVATIVES OF MANGANESE CARBONYL CONTAINING A CARBON–MANGANESE σ-BOND

1. Alkyl- and Acyl-manganese Pentacarbonyls

Like acids, hydrogen carbonylmanganates are able to react with various alkylating agents to form compounds in which the carbon atom is attached directly to the metal atom. The relatively high stability of these compounds can be explained by the influence of the carbonyl groups on the organic substituents[82].

The simplest organic derivative of manganese carbonyl, pentacarbonylmethylmanganese, can be obtained by the action of diazomethane on hydrogen carbonylmanganate[52,83]:

$$CH_2N_2 + HMn(CO)_5 \rightarrow CH_3Mn(CO)_5 + N_2.$$

Other methylating agents, e.g. dimethyl sulphate[84], can be used besides diazomethane.

Higher alkylmanganese pentacarbonyls can be obtained by the reaction of hydrogen pentacarbonylmanganate with alkenes[85]:

$$CH_2—CH=CH_2 + HMn(CO)_5 \rightarrow CH_3CH_2CH_2—Mn(CO)_5.$$

A method which has found some application for the preparation of alkyl derivatives of manganese carbonyl involves the use of organic derivatives of the alkali metals or of Grignard reagents[52]:

$$C_4H_9Li + BrMn(CO)_5 \rightarrow C_4H_9—Mn(CO)_5 + LiBr.$$

A method based on the reaction of alkali-metal pentacarbonylmanganates with organic halides[83,86]

$$R—X + NaMn(CO)_5 \rightarrow R—Mn(CO)_5 + NaX$$

is most often used. It is possible to obtain only the simplest carbonylalkylmanganese compounds by means of this reaction, since beginning with the isopropyl halides the reaction leads to the formation of halogenopentacarbonylmanganese derivatives, e.g. [50]

$$2\,C_4H_9Br + 2NaMn(CO)_5 \rightarrow 2BrMn(CO)_5 + 2NaBr + C_8H_{18}.$$

However, this method is widely used to obtain alkenyl derivatives of manganese carbonyl[91,92], and also for the synthesis of pentacarbonylacylmanganese derivatives[87]:

$$R—\overset{\overset{O}{\|}}{C}—Cl + NaMn(CO)_5 \rightarrow R—\overset{\overset{O}{\|}}{C}—Mn(CO)_5 + NaCl$$

which when heated to 100–120°C are readily converted into pentacarbonylalkylmanganese compounds:

$$R—CO—Mn(CO)_5 \rightarrow R—Mn(CO)_5 + CO.$$

Numerous alkyl and acyl derivatives of manganese carbonyl have been prepared by all the above methods. Aromatic[93] and heteroaromatic[88,94–96] derivatives can also be obtained by such methods:

$$C_6H_5Cl + NaMn(CO)_5 \rightarrow C_6H_5—Mn(CO)_5 + NaCl$$

as well as compounds containing two pentacarbonylmanganese groups separated by a chain of carbon atoms[89,90]:

$$Cl—(CH_2)_8—Cl + 2NaMn(CO)_5 \rightarrow (CO)_5Mn—(CH_2)_8—Mn(CO)_5 + 2NaCl$$

$$R(COCl)_2 + 2NaMn(CO)_5 \xrightarrow[-2NaCl]{} R—[CO—Mn(CO)_5]_2 \xrightarrow[-2CO]{} R[Mn(CO)_5]_2.$$

Organic derivatives of manganese carbonyl containing a carbon–manganese σ-bond are usually stable towards oxygen and moisture, but on prolonged storage they slowly decompose with the evolution of carbon monoxide. On treatment with halogens the organic radical is replaced by a halogen atom:

$$R—Mn(CO)_5 + Br_2 \rightarrow RBr + BrMn(CO)_5.$$

Concentrated hydrohalic acids act similarly.

Calderazzo and Noack[97] investigated the reaction between lithium iodide and pentacarbonylmethylmanganese, in which one carbonyl group is replaced by an iodine atom, and is then incorporated between the methyl group and the manganese atom:

$$CH_3—Mn(CO)_5 + LiI \rightarrow Li[CH_3CO—Mn(CO)_4I].$$

This reaction is a particular case of the addition to organomanganese pentacarbonyls of ligands which possess a lone pair of electrons, e.g. carbon monoxide, triphenylphosphine,, amines, etc. The ligand displaces one carbonyl group, which is incorporated between the alkyl group and the metal atom:

$$R—Mn(CO)_5 + L \rightarrow RCO—Mn(CO)_4L.$$

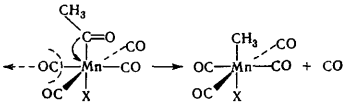
The addition of carbon monoxide (carbonylation) and that of triphenylphosphine have been studied in the greatest detail.

The carbonylation reaction

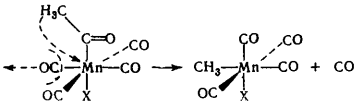
$$R-Mn(CO)_5+CO\rightleftarrows R-CO-Mn(CO)_5,$$

discovered by Coffield et al.[87] in 1957, is reversible: acylmanganese carbonyls when heated to 100°C are converted into the corresponding alkyl derivatives. It was shown with labelled carbon monoxide[98] that in the carbonylation the free carbon monoxide molecule is not immediately incorporated between the alkyl radical and the manganese atom, and in the reverse reaction the liberated carbonyl group also was not initially linked with the alkyl radical.

Mawby et al.[99] point out two alternative mechanisms for the decarbonylation of acyl derivatives of manganese carbonyl—(*a*) carbonyl insertion



or (*b*) migration of the alkyl group



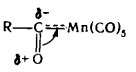
It has not yet proved possible to establish precisely which of these two mechanisms is correct. However, in the carbonylation of complexes of the type $RMn(CO)_4X$, where X is some ligand other than carbonyl, these mechanisms yield different products. If the reaction involves alkyl migration, the product should have a *cis*-configuration; in the contrary case a *trans*-isomer should be formed.

From a study of the decarbonylation of *trans*-tetracarbonyltriphenylphosphineacetylmanganese Mawby et al.[90] concluded that an alkyl migration mechanism (*b*) is to be preferred. Addition to alkylmanganese pentacarbonyls of phosphines and secondary amines[100,101] and other reactions involving incorporation of a carbonyl group between a manganese atom and an alkyl radical probably occur by the same mechanism.

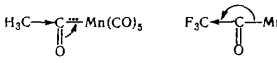
The rate of carbonylation of a pentacarbonylalkylmanganese depends on the nature of the organic radical. Calderazzo and Cotton showed that the rate of carbonylation decreases in the sequence[102]

$$n\text{-}C_3H_7\gtrsim C_2H_5>C_6H_5>CH_3\gg C_6H_5CH_2\simeq CF_3.$$

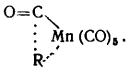
The ease of conversion of alkyl derivatives of manganese carbonyl into the corresponding acyl derivatives and of the reverse reaction indicates that the acyl carbonyl group has a special character. Although the infrared spectra of the acyl derivatives contain an absorption band in the range 1590–1640 cm^{-1}, corresponding to the carbonyl absorption band in aldehydes and ketones, the acyl carbonyl exhibits none of the chemical properties characteristic of a ketonic or an aldehydic carbonyl group. Its specific character is probably due to an increase in electron density on the carbon atom resulting from the positive inductive effect of the pentacarbonylmanganese group. Some levelling out of all the manganese–carbon bonds in the pentacarbonylacylmanganese molecules, owing to the formation of a dative π-bond between the manganese and the acyl carbon atom



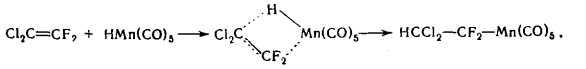
may also be assumed. The presence of strong electron-acceptor groups in the organic radical will prevent an increase in the multiplicity of the Mn=C bond, and thereby tend to strengthen the C–R bond and impede decarbonylation:



It may further be supposed that pentacarbonylacylmanganese molecules will contain a seven-coordinated manganese atom



Complexes of this type have recently been prepared[103]. The hypothesis of seven-coordinated manganese complexes provides an explanation not only for the mechanism of the decarbonylation of acyl derivatives of manganese carbonyl but also for the addition of unsymmetrical halogenated alkenes to hydrogen carbonylmanganate, which under normal conditions involves the formation of only one isomer:



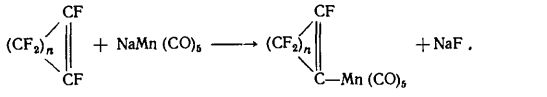
2. Perfluoro-derivatives

A large number of papers have recently been published on perfluoroalkylmanganese pentacarbonyls. The interest taken in these compounds is due to their great stability in comparison with their hydrocarbon analogues, this being an effect of the electronegative fluorine atoms.

Perfluoro-derivatives of manganese carbonyl can be obtained by all the general methods described above for the synthesis of alkyl and aryl derivatives[104]. Methods using organometallic compounds have acquired relatively greater value[105,106]:

$$BrMn(CO)_5+LiC_6F_5\rightarrow C_6F_5-Mn(CO)_5+LiBr$$
$$BrMn(CO)_5+C_6F_5MgBr\rightarrow C_6F_5-Mn(CO)_5+MgBr_2.$$

Certain methods for obtaining perfluoroalkyl derivatives of manganese carbonyl are specific. Thus when perfluorocycloalkenes react with the pentacarbonylmanganate anion, a fluorine atom adjacent to the double bond is replaced by $Mn(CO)_5$ [107,108]:



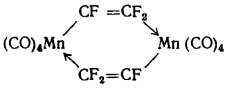
An extremely interesting reaction between perfluoroethylene and compounds containing a tin–manganese bond was accomplished by Clark and Tsai[109]. It involved incorporation of the tetrafluoroethylene molecule in the tin–manganese bond:

$$(CH_3)_3Sn-Mn(CO)_5+CF_2=CF_2\rightarrow(CH_3)_3Sn-CF_2-CF_2-Mn(CO)_5.$$

The resulting compound readily decomposed with the separation of an organomanganese dimer:

$$2[(CH_3)_3Sn-CF_2-CF_2-Mn(CO)_5]\rightarrow 2(CH_3)_3SnF+[CF_2=CF-Mn(CO)_4]_2+2CO$$

which, in the opinion of these workers, had the "bridge" structure



The infrared absorption spectra of these compounds have been studied in great detail[110-114]. There are also data on the ^{19}F n.m.r. spectra of several of these compounds[114-116].

The chemical properties of the perfluoroalkyl and perfluoroacyl derivatives of manganese pentacarbonyl do not in general differ from those of their hydrocarbon analogues[117-121].

VI. HALOGENO-CARBONYLS AND ALLIED COMPOUNDS

1. Halogeno-derivatives of Manganese Carbonyl

Decacarbonyldimanganese reacts with halogens to form halogenomanganese carbonyls[122]:

$$[Mn(CO)_5]_2 + Cl_2 \rightarrow 2ClMn(CO)_5,$$

Other methods for obtaining these compounds are the reactions of alkyl- and acyl-manganese pentacarbonyls with halogens[89]:

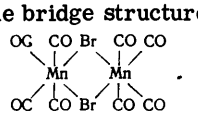
$$Mn(CO)_5R + Br_2 \rightarrow RBr + BrMn(CO)_5$$
$$RCO{-}Mn(CO)_5 + I_2 \rightarrow RCOI + IMn(CO)_5$$

and also heating decacarbonyldimanganese with carbon tetrachloride, chloroform, and other halogenated hydrocarbons under ultraviolet irradiation[42].

Halogenomanganese carbonyls are stable towards moisture and atmospheric oxygen at room temperature. On heating, carbon monoxide is gradually eliminated, with the formation of dimeric halogeno-carbonyls:

$$2Mn(CO)_5X \rightarrow [Mn(CO)_4X]_2 + 2CO.$$

These dimers have the bridge structure[123]



The Mn–Br distance is 2.526 ± 0.005 Å, and the Mn...Mn distance is 3.74 Å, which considerably exceeds the Mn–Mn distance in the decacarbonyldimanganese molecule.

A kinetic study has been made of isotope between exchange halogenomanganese pentacarbonyls and carbon monoxide[40,124]:

$$XMn(CO)_5 + C^*O \rightleftarrows XMn(CO)_4(C^*O) + CO.$$

The rate of exchange of carbon monoxide is found to depend on the atomic radius of the halogen: in the series—chlorine, bromine, iodine—the intensity of exchange diminishes in the proportions 200 : 8 : 1.[40]

The addition of a halogen atom to the pentacarbonylmanganese group makes the carbonyl group somewhat more mobile than in the original decacarbonyldimanganese. Halogenomanganese carbonyls interact with various ligands (L) possessing a lone pair of electrons, with replacement of one or two carbonyl groups:

$$XMn(CO)_5 + L \rightarrow LMn(CO)_4X + CO,$$
$$XMn(CO)_5 + 2L \rightarrow L_2Mn(CO)_3X + 2CO.$$

Besides the carbonyl group the halogen atom may also be replaced[125]:

$$BrMn(CO)_5 + 2KCN \rightarrow K[Mn(CO)_4(CN)_2] + CO + KBr.$$

The infrared spectra of halogenomanganese pentacarbonyls[126-128] support the hypothesis that the axial carbonyl in the pentacarbonylmanganese group is more firmly bound than are the equatorial groups to the manganese atom.

2. Nitrato- and Thiocyanato-compounds

Addison et al.[129,130] prepared stable nitratopentacarbonylmanganese by the reaction of decacarbonyldimanganese with dinitrogen tetroxide:

$$Mn_2(CO)_{10} + N_2O_4 \rightarrow Mn(CO)_5NO_3.$$

This compound consists of pale yellow crystals, and decomposes when heated in a vacuum above 55 °C. It is soluble in polar solvents, but insoluble in carbon disulphide and aliphatic hydrocarbons. It is easily solvated in solution, with the formation of $[Mn(CO)_5Solv]^+NO_3^-$ complexes. The infrared spectrum of this compound confirms the presence of both carbonyl groups (ν_{CO} = 2060 and 2002 cm^{-1}) and a nitrato-group (ν_{NO_3} = 1486, 1284, 1010, and 805 cm^{-1}) attached to the manganese atom.

Farona and Wojcicki[131,132] prepared thiocyanatopentacarbonylmanganese by the reaction of sodium pentacarbonylmanganate with thiocyanogen chloride:

$$NaMn(CO)_5 + ClSCN \rightarrow Mn(CO)_5SCN + NaCl$$

obtaining golden-yellow crystals decomposing at 156 °C and soluble in polar solvents. In air this compound is stable in the dark, but slowly decomposes in the light. It reacts with electron-donor ligands, e.g. triphenylphosphine or pyridine, with replacement of carbonyl groups:

$$Mn(CO)_5SCN + 2C_5H_5N \rightarrow Mn(CO)_3(C_5H_5N)_2SCN + 2CO.$$

It is noteworthy that the reaction between decacarbonyldimanganese and bithiocyanogen $(SCN)_2$ yields a polymeric compound instead of the expected thiocyanatopentacarbonylmanganese.

VII. PRODUCTS RESULTING FROM SUBSTITUTION OF CARBONYL GROUPS

Reactions involving the replacement of carbonyl groups are widespread in the chemistry of metal carbonyls. Carbon monoxide can easily be substituted by various ligands possessing electron-donor properties. Substitution of a carbonyl group in derivatives of manganese pentacarbonyl is not usually accompanied by change in the oxidation state of the metal atom. Complete replacement of all the carbonyl groups is rare, only one or two of them usually being replaced. This is probably due to the increase in stability of the manganese–carbon bond on introduction of an electron-donor ligand, consequent on an increase in the statistical weight of structures of the type[133,134]

$$L{-}M{=}C{=}O \longleftrightarrow L^+{-}M{\equiv}C{-}O^-.$$

1. Isocyanide and Nitrile Complexes

Isocyanides R.N:C are the closest analogues of carbon monoxide, and therefore they should readily displace the latter from metal carbonyls. However, complete replacement of carbonyl groups by alkyl isocyanide groups has been accomplished only with nickel tetracarbonyl[135]. In derivatives of manganese carbonyl only two carbonyl groups can be replaced[125]:

$$BrMn(CO)_5 + 2R{-}N{=}C \rightarrow BrMn(CO)_3(CNR)_2 + 2CO.$$

Further substitution of carbon monoxide is not prevented by instability of the isocyanide complexes, since

ionic isocyanide complexes of manganese are known[136] which do not contain carbonyl groups:

$$MnI_2 + 6R{-}N{=}C \rightarrow [Mn(CNR_6]I.$$

Furthermore, Pauson and Stubbs[137] obtained an isocyanide analogue of tricarbonylcyclopentadienylmanganese:

$$C_5H_5Mn(CO)_3 + 3\,C_6H_5NC \rightarrow C_5H_5Mn(CN{-}C_6H_5)_3 + 3CO$$

this being a stable crystalline substance melting at 97°C. Thus available data suggest that the difficulty of further replacement of carbonyl by isocyanide groups is associated with enhanced stability of the manganese–carbon bonds.

Products have also been obtained in which carbonyl groups in derivatives of manganese carbonyl have been replaced by cyano-groups[125]:

$$BrMn(CO)_5 + KCN \rightarrow K[Mn(CO)_4(CN)_2] + KBr.$$

2. Nitrosyl Derivatives of Manganese Carbonyl

Nitrosyl derivatives of manganese carbonyl can be obtained by the action of nitric oxide on the halogeno-carbonyls[138,139]:

$$Mn(CO)_5I + NO \rightarrow Mn(CO)_4NO + Mn(CO)(NO)_3.$$

Tetracarbonylnitrosylmanganese $Mn(CO)_4NO$ is a pale yellow liquid (m.p. between −1.5° and 0°C), while carbonyltrinitrosylmanganese $MnCO(NO)_3$ is a crystalline substance melting at 27°C. The infrared spectra of these compounds were studied by Beck and Lottes[140].

The carbonyl groups in the mixed carbonyl–nitrosyl complexes of manganese can be further replaced by various ligands:

$$Mn(NO)_3CO + P(C_6H_5)_3 \rightarrow Mn(NO)_3P(C_6H_5)_3 + CO.$$

Another method for obtaining products in which the carbonyl groups have been completely replaced is the action of nitric oxide on substituted derivatives of manganese carbonyl[141–143]:

$$LMn(CO)_4 + NO \rightarrow LMn(NO)_3 + LMn(CO)_3NO$$

where L = $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, etc.

A halogen derivative of manganese nitrosyl was obtained[144] by the reaction between iodotetracarbonyl(triphenyl phosphite)manganese and nitric oxide:

$$Mn(CO)_4P(OC_6H_5)_3I + NO \rightarrow Mn(NO)_2[P(OC_6H_5)_3]_2I + MnI_2 + CO.$$

3. Substitution of Carbonyl Groups by Nitrogen Compounds

Besides compounds containing multiple-bonded nitrogen, whose reactions with derivatives of manganese carbonyl have been described above, replacement of carbonyl groups can occur also with compounds in which the nitrogen atom possesses a lone pair of electrons, e.g. amines, pyridine, etc.

Ammonia reacts with bromopentacarbonylmanganese at 70°C and 35 atm to form $Mn(NH_3)_3(CO)_3Br$ (decomposing at ~ 190°C). The corresponding chloride and iodide have been obtained in analogous fashion, as well as the compounds $Mn(NH_3)_2(CO)_4Br$[125]† and $[Mn(NH_3)_3(CO)_3]^+[Mn(CO)_5]^-$.[146]

† This should probably be Ref. 145 (Ed. of Translation).

A similar reaction takes place with various amines[125,147–150]:

$$XMn(CO)_5 + R'NR''_2 \rightarrow Mn(CO)_3(NR'R''_2)_2X + CO.$$

Quaternary ammonium salts react with halogenomanganese pentacarbonyls forming crystalline salts[151]:

$$R_4N^+X^- + XMn(CO)_5 \rightarrow R_4N^+[Mn(CO)_4X_2]^- + CO.$$

The same products are obtained by the action of quaternary ammonium salts on dinuclear halogenomanganese carbonyls:

$$2\,R_4N^+X^- + [Mn(CO)_4X]_2 \rightarrow 2\,R_4N^+[Mn(CO)_4X_2]^-.$$

With decacarbonyldimanganese this reaction yields the complex $(R_4N)_2[MnX(CO)_4]_2$.

Angelici has recently reported[103] the preparation of products of the addition of primary amines to bromopentacarbonylmanganese:

$$3\,RNH_2 + BrMn(CO)_5 \rightarrow Mn(CO)_5(NHR)(NH_2R) + RNH_3^+Br^-$$

(where R = CH_3, iso-C_3H_7, n-C_4H_9, t-C_4H_9, cyclohexyl, or RNH_2 = ethylenediamine). Diamagnetic compounds have been isolated as a result of these reactions. If the structure proposed for the compounds is correct, they constitute the first example of stable complexes of manganese carbonyl having a coordination number of seven, in which the number of electrons around the manganese exceeds the number around the krypton atom.

4. Phosphorus, Arsenic, and Antimony Derivatives

The most thorough study has been made of products obtained by replacing carbonyl groups in derivatives of manganese carbonyl by various alkylated and arylated phosphines, arsines, and stibines. These compounds are readily formed by the direct interaction of decacarbonyldimanganese, or its derivatives, e.g. the halogeno-derivatives, with the ligands[125,152,153]:

$$XMn(CO)_5 + AR_3 \rightarrow Mn(CO)_4X \cdot AR_3 + CO$$

$$XMn(CO)_4X \cdot AR_3 + AR_3 \rightarrow Mn(CO)_3X(AR_3)_2 + CO$$

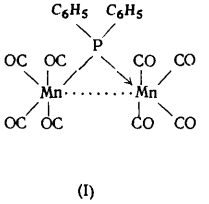
where X = Cl, Br, I; A = P, As, Sb; and R = Alk, Ar.

Angelici and Basolo established[154] the dependence of the rate of substitution of carbonyl groups on the nature of the ligand as $(C_6H_5)_3P > (C_6H_5)_3As \simeq (C_4H_9)_3P \simeq (C_6H_5)_2PCl > (C_6H_5O)_3P \simeq (C_6H_5)_3Sb > C_6H_5PCl_2 \simeq (C_4H_9O)_3P > CH_3C(CH_2O)_3P$.

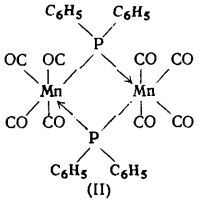
Exposure to ultraviolet radiation during replacement of the carbonyl groups results in the formation of dimeric products[155,156]:

$$Mn_2(CO)_{10} + 2AR_3 \xrightarrow{h\nu} [Mn(CO)_4AR_3]_2 + 2CO.$$

This reaction probably takes place in stages. Green and Moelwyn-Hughes[157] were able to isolate, from the reaction between diphenylphosphinous chloride and sodium pentacarbonylmanganate, two products of the stepwise replacement of carbon monoxide, to which they ascribed the structures

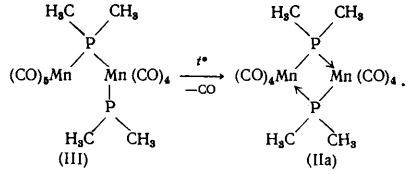


(I)



(II)

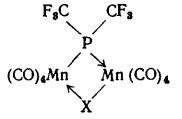
It was shown later[158] that the "doubly bridged" compound (IIa) is formed via the intermediate carbonyl complex (III), which contains only one "bridging" dimethylphosphino-group:



Dinuclear perfluoromethylated phosphine and arsine derivatives of manganese carbonyl have been prepared[159-161] by the reaction

$$[Mn(CO)_5]_2 + (CF_3)_2AX \rightarrow Mn_2(CO)_8A(CF_3)_2X + 2CO$$
(IV)

where A = P, As and X = Cl, Br, I, SCF_3, $SeCF_3$, $(CF_3)_2P$. Complexes of this type probably have the "doubly bridged" structure



In contrast to them, the compound $Mn_2(CO)_9P(CF_3)_2N(CH_3)_2$, obtained by the reaction between decacarbonyldimanganese and dimethylaminobistrifluoromethylphosphine[161], contains no "bridging" phosphine groups. It probably has the linear structure

$$(CO)_5Mn—Mn(CO)_4—P(CF_3)_2—N(CH_3)_2.$$

Decacarbonyldimanganese reacts with *o*-phenylenebis-dimethylarsine at an elevated temperature[162,163] to form the diamagnetic dimeric product

$$\{Mn(CO)_3[(CH_3)_2As—C_6H_4—As(CH_3)_2]\}_2$$

which on further heating passes into a paramagnetic monomer:

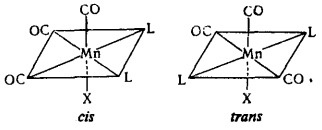
$$\{Mn(CO)_3[diars]\}_2 \rightarrow 2Mn(CO)_3[diars]$$
$$diars = o\text{-}(CH_3)_2AsC_6H_4As(CH_3)_2.$$

The dimeric complex reacts in chloroform with free halogens:

$$\{Mn(CO)_3[diars]\}_2 + Cl_2 \rightarrow 2Mn(CO)_3[diars]Cl.$$

Excess of halogen produces a gradual replacement of carbonyl groups with the formation of $Mn(CO)_2[diars]Cl_2$ and $Mn[diars]Cl_3$. Analogous compounds have been obtained from decacarbonyldimanganese and ethylene-1,2-bisdiphenylphosphine[164-166].

Mononuclear compounds of general formula $Mn(CO)_3L_2X$ can exist in the form of the stereoisomers[167-169]



cis *trans*

The relative proportions of *cis*- and *trans*-isomers formed as a result of the stepwise substitution of carbonyl groups depends on the nature of the added ligand. Thus the replacement of carbonyl groups by triphenylphosphine yields mainly the *trans*-isomer, whereas the pyridine complex exists solely in the *cis*-form[167,168]. The stability of a particular stereoisomer probably depends primarily on steric factors.

The chemical properties of the phosphine-substituted derivatives of manganese carbonyl and their arsine and stibine analogues are fundamentally similar to those of manganese carbonyl itself and its other derivatives[169,170]. These compounds react with sodium amalgam to form the corresponding salts:

$$Mn(CO)_4LX + 2Na \xrightarrow{Hg} NaMn(CO)_4L + NaX$$

$$Mn(CO)_3L_2X + 2Na \xrightarrow{Hg} NaMn(CO)_3L_2 + NaX$$

which can be used to prepare various alkyl and acyl derivatives:

$$NaMn(CO)_3L_2 + (RCO)_2O \rightarrow RCO—Mn(CO)_3L_2 + RCOONa.$$

On being heated, acyl derivatives are also capable of conversion into alkyl derivatives, with the loss of a molecule of carbon monoxide:

$$RCO—Mn(CO)_3L_2 \rightarrow R—Mn(CO)_3L_2 + CO.$$

Hydrolysis of sodium tetracarbonyltriphenylphosphine-manganate yields the corresponding hydrogen compound[170]:

$$NaMn(CO)_4P(C_6H_5O)_3 + H^+ \rightarrow HMn(CO)_4P(C_6H_5O)_3.$$

The sodium salts can be used for the preparation of mercury derivatives of manganese carbonyl:

$$2NaMn(CO)_4PR_3 + Hg(CN)_2 \rightarrow [Mn(CO)_4PR_3]_2Hg + 2NaCN.$$

Analogous mercury derivatives were obtained also from manganese carbonyl compounds containing two ligand molecules:

$$2NaMn(CO)_3[P(C_6H_5)_3]_2 + Hg(CN)_2 \rightarrow \{Mn(CO)_3[P(C_6H_5)_3]_2\}_2Hg + 2NaCN.$$

5. Compounds containing Sulphur and Tellurium

The first derivative of manganese carbonyl containing a manganese–sulphur bond was prepared by Hieber and Schropp[125] by the reaction

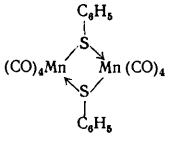
$$ClMn(CO)_5 + C_6H_5SH \rightarrow [Mn(CO)_4—S—C_6H_5]_2.$$

This reaction was subsequently applied to decacarbonyldimanganese[171,172]:

$$R—SH + Mn_2(CO)_{10} \rightarrow 2RS—Mn(CO)_5$$

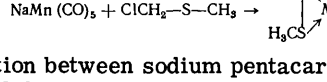
where R = C_2H_5, C_3H_7, C_6H_5, *p*-$CH_3C_6H_4$.

Reaction between manganese carbonyl and compounds containing two sulphur atoms (1,2-diphenylthioethane[164], dithian[173], etc.) has been used to synthesise dinuclear "bridged" compounds



resembling the dinuclear compounds containing phosphine or arsine.

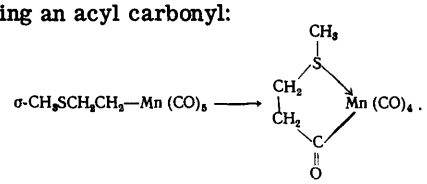
King and Bisnette[174] prepared compounds in which the sulphur atom was attached to the manganese atom by a π-bond:



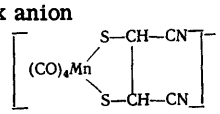
Interaction between sodium pentacarbonylmanganate and alkyl halides containing sulphur initially produces a compound containing a σ-bond:

$$NaMn(CO)_5 + ClCH_2CH_2—S—CH_3 \rightarrow \sigma\text{-}CH_2SCH_2CH_2—Mn(CO)_5 + NaCl$$

and this on ultraviolet irradiation passes into a π-derivative containing an acyl carbonyl:



Finally, the complex anion



in which the manganese atom is attached to two sulphur atoms, has been obtained[175] by the reaction between bromotetracarbonyltriphenylphosphinemanganese and sodium *cis*-1,2-dicyanoethane-1,2-dithiolate.

Derivatives of manganese pentacarbonyl containing the manganese–tellurium[176] and the manganese–selenium bonds can be prepared by similar methods.

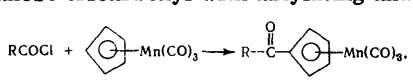
VIII. π-HYDROCARBON MANGANESE CARBONYL DERIVATIVES

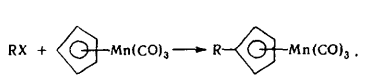
Besides the organic derivatives of manganese carbonyl described in Section V, in which the carbon atom is bound to the metal atom by a σ-bond, several compounds are known in which the π-electrons of carbon atoms effect the link between the manganese atom and a hydrocarbon group. As in other "sandwich" compounds, a π-bond between an organic group and a pentacarbonylmanganese group is possible only when the ligand has a coplanar configuration[177].

The most thoroughly studied π-complex of manganese carbonyl is cyclopentadienylmanganese tricarbonyl $C_5H_5Mn(CO)_3$. Several methods are now known for preparing it, one of the most convenient being the reaction between halogenomanganese pentacarbonyls and cyclopentadienyl-sodium[178] or -thallium[179]:

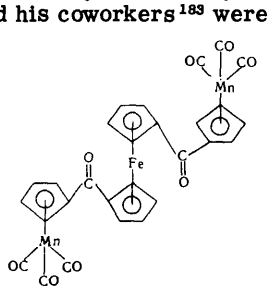
$$C_5H_5Na + BrMn(CO)_5 \rightarrow C_5H_5Mn(CO)_3 + 2CO + NaBr.$$

The chemistry of cyclopentadienylmanganese tricarbonyl and its derivatives has been described in detail[180,181], and therefore we shall mention only certain reactions of this compound. Various substituents can be introduced into the cyclopentadienyl ring by interaction of cyclopentadienylmanganese tricarbonyl with alkylating and acylating agents[182]:





The most diverse compounds containing a tricarbonylmanganese group have been synthesised by this method. For example, Cais and his coworkers[183] were able to obtain the compound



which contains a ferrocene "sandwich" besides tricarbonylmanganese groups.

The cyclopentadienyl ring in the cyclopentadienylmanganese tricarbonyl molecule exhibits all the properties characteristic of aromatic systems. At the same time the presence of carbonyl groups attached to the metal atom enables reactions typical of metal carbonyls to be carried out, e.g. the replacement of carbonyl groups by electron-donor ligands[184]:

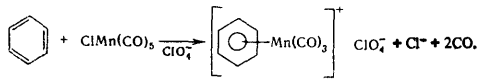
$$C_5H_5Mn(CO)_3 + (CH_3)_2NH \rightarrow C_5H_5Mn(CO)_2NH(CH_3)_2 + CO$$

$$C_5H_5Mn(CO)_3 + P(C_6H_5)_3 \rightarrow C_5H_5Mn(CO)_2P(C_6H_5)_3 + CO.$$

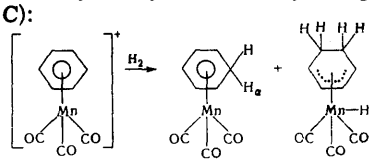
Strohmeier and von Hobe[185] replaced carbon monoxide in cyclopentadienyl tricarbonyl by diphenylacetylene:

$$C_5H_5Mn(CO)_3 + C_6H_5C{\equiv}CC_6H_5 \rightarrow C_5H_5Mn(CO)_2(C_6H_5C{\equiv}CC_6H_5) + CO.$$

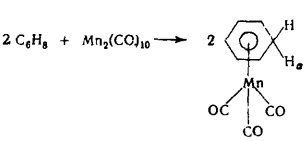
Aromatic systems other than the cyclopentadienyl ring are also able to form π-complexes with manganese carbonyl[185]. Hydrocarbons of the benzene series form either complexes of the type π-Ar–$Mn(CO)_4$ [186] or cations $[\pi\text{-Ar–}Mn(CO)_3]^+$. For example, benzene reacts with chloropentacarbonylmanganese in the presence of Friedel–Crafts catalysts according to the equation



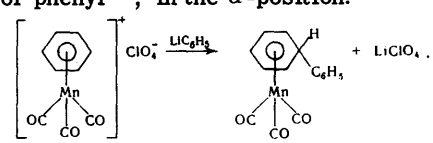
Reduction of this cation with sodium tetrahydroborate[188] or with hydrogen over Raney nickel yields π-cyclohexadienemanganese tricarbonyl (m.p. 78°C) and small amounts of hydrogen tricarbonyl-π-cyclohexadienylmanganate (decomposes at 95°C):



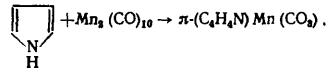
The first of these compounds can also be readily obtained by the interaction of decacarbonyldimanganese with cyclohexadiene[189]:



The benzenetricarbonylmanganese cation can be stabilised also by the addition of various substituents, e.g. methyl[190] or phenyl[191], in the α-position:

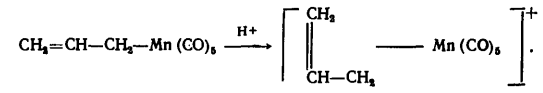


Joshi et al.[192,193] synthesised several derivatives of heterocyclic compounds and manganese carbonyl containing a π-bond:

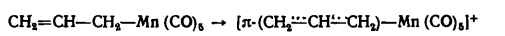


Not only aromatic systems but also various unsaturated acyclic systems are able to form π-complexes with manganese carbonyl. It is supposed that the pentacarbonylethylenemanganese cation, which has already been discussed (Section IV, 2), formed by the reaction of ethylene with manganese carbonyl[56], and also by detachment of a

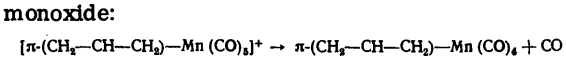
proton from ethylmanganese pentacarbonyl by the action of triphenylmethyl tetrafluoroborate[194], is a π-complex. It has been found[195] that an analogous cation is formed by the action of perchloric acid on σ-allylmanganese pentacarbonyl:



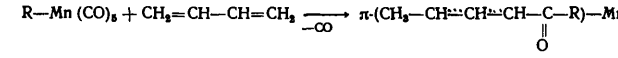
Stable π-allyl complexes of manganese carbonyl have been obtained by heating the corresponding σ-alkyl derivatives $R-Mn(CO)_5$ while exposed to ultraviolet radiation[85,92,196]. This reaction probably involves the intermediate formation of an unstable cation:



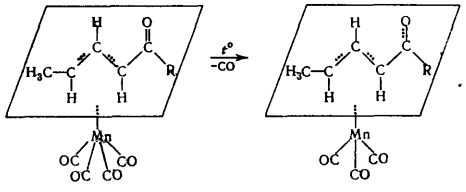
which is then stabilised by eliminating a molecule of carbon monoxide:



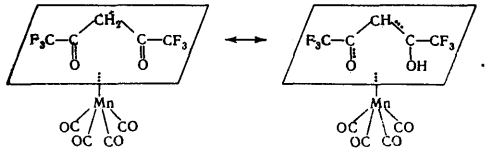
Analogous π-complexes have been obtained by interaction between dienes and alkyl or aryl derivatives of manganese pentacarbonyl[197]:



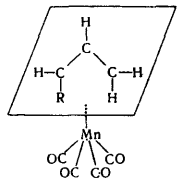
When such a compound (R = C_6H_5) is heated above 110°C, a molecule of carbon monoxide is split off, stabilisation of the resulting tricarbonyl complex probably being due to interaction of the π-orbitals of the ketonic carbonyl with *d*-electrons of the manganese atom:



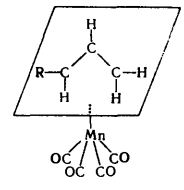
Similar formation of a π-bond by π-electrons of an acyl carbonyl is probably observed also in tetracarbonylhexafluoropentane-2,4-dionemanganese, which was prepared by Kilner and Wojcicki[198]:



π-Allyl compounds of maganese carbonyl are distinguished from the corresponding σ-allyl complexes primarily by the coplanar arrangement of the carbon atoms in the organic portion of the molecule. Some workers postulate[192,193] that the higher homologues of π-allyl derivatives of manganese carbonyl may exist as different stereoisomers



anti-1-alkyl-π-allylmanganese tetracarbonyl



syn-1-alkyl-π-allylmanganese tetracarbonyl

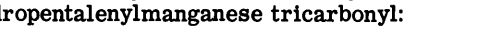
However, such a hypothesis is hardly justified, since such isomers are absent from the "sandwich" compounds, e.g. ferrocene and cyclopentadienylmanganese tricarbonyl, which are allied to the π-allyl complexes of manganese carbonyl[199].

The π-allyl complexes are rather more stable than the corresponding σ-allylmanganese pentacarbonyls. Their boiling (melting) points are usually higher than those of compounds containing a σ-bond. The infrared absorption spectra and the nuclear magnetic resonance spectra indicate that single and double bonds in the organic substituents are levelled out. The accompanying Table gives for comparison some physicochemical characteristics of σ- and π-allylmanganese carbonyls.

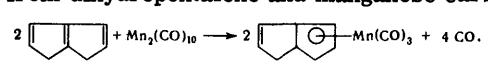
Physicochemical properties of σ- and π-allylmanganese carbonyls.

Property	σ-CH_2=$CHCH_2Mn(CO)_5$	π-$(CH_2$=$CHCH_2)$—$Mn(CO)_4$
State	Liquid	Crystals
Melting (boiling) point, °C	25/10^{-3}	55—56
Infrared absorption spectrum, cm^{-1}		
ν C=C	1620	1505
ν C=O	2110, 2079, 2024, 2004	2110, 2060, 2049, 1950
N.m.r. spectrum, τ, p.p.m.	6.14 (sextet) 4.68 (triplet) 1.81 (doublet)	4.80 (sextet) 2.76 (doublet) 1.77 (doublet)

Finally, we must deal with the very peculiar reaction between manganese carbonyl and acetylene[200-202], by means of which the most diverse derivatives of cyclopentadienylmanganese tricarbonyl can be obtained. At 150°C and 40–45 atm acetylene forms with decacarbonyldimanganese or with methylmanganese pentacarbonyl the compound π-dihydropentalenylmanganese tricarbonyl:

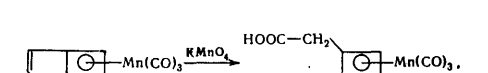


The same compound was obtained by Riemschneider[201] directly from dihydropentalene and manganese carbonyl:

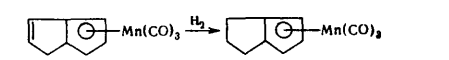


Analogous complexes have been obtained from azulene and indene[203-205].

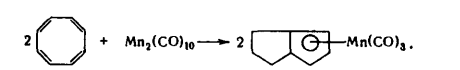
The oxidation of π-dihydropentalenylmanganese tricarbonyl yields cyclopentadienylmanganese tricarbonyl derivatives:



Reduction over Raney nickel results in a π-tetrahydropentalenyl derivative[206]:



which can be prepared also from manganese carbonyl and cyclo-octatetraene:



IX. COMPOUNDS CONTAINING A BORON ATOM

With most boron compounds manganese carbonyl can react only as a donor of electrons. Thus interaction of the borane–ether complex with sodium pentacarbonylmanganate gave[207] the unstable complex $[(C_2H_5)_4N]^+[H_3B{-}Mn(CO)_5]^-$, which decomposes with the evolution of diborane even at −25°C. A complex in which one carbonyl group had been replaced by triphenylphosphine

$$[H_3B{-}Mn(CO)_4P(C_6H_5)_3]^-[(C_2H_5)_4N]^+$$

was synthesised in an analogous fashion. Nöth and Schmidt[208] isolated several compounds containing a boron–manganese σ-bond, in which the boron atom was attached to a dimethylamino-group or a chlorine or bromine atom.

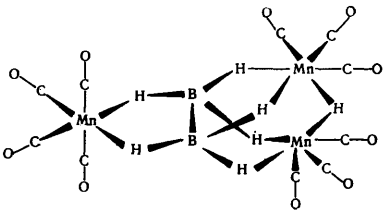
Reaction between diphenyl- or di-n-butyl-boron chloride and sodium pentacarbonylmanganate results in complete elimination of carbonyl groups with the formation of compounds of the type $(R_2B{-}Mn)_2$.

Ionic complexes of manganese carbonyl derivatives have also been obtained containing the tetrafluoroborate anion[194]:

$$C_2H_5Mn(CO)_5 + (C_6H_5)_3C^+BF_4^- \rightarrow [C_2H_4{-}Mn(CO)_5]^+BF_4^-$$

$$[C_2H_4{-}Mn(CO)_5]^+BF_4^- + P(C_6H_5)_3 \rightarrow [(C_6H_5)_3P]_2Mn(CO)_4]^+BF_4^- .$$

An interesting complex of a hydroboron with manganese carbonyl $B_2H_7Mn_3(CO)_{10}$ has recently been synthesised[209]. It is stable only in the absence of air. Electron diffraction has shown that the manganese and boron atoms are linked by hydrogen bonds:



The boron–manganese distances in this compound are 2.30 ± 0.02 Å, the boron–boron bond length is 1.76 ± 0.03 Å, and the manganese atoms are only 2.845 ± 0.003 Å apart. We may recall that the manganese–manganese bond length in the decacarbonyldimanganese molecule is 2.923 ± 0.003 Å.

An organoboron analogue of cyclopentadienylmanganese tricarbonyl has recently been synthesised[210]:

$$B_9C_2H_{11}Cs_2 + BrMn(CO_5) \xrightarrow{\text{rapid}} [B_9C_2H_{11}Mn(CO)_5]^- + 2\,CsBr$$

$$[B_9C_2H_{11}Mn(CO)_5]^- \xrightarrow{\text{slow}} [B_9C_2H_{11}Mn(CO)_3]^- + 2CO .$$

X. APPLICATIONS OF MANGANESE CARBONYL DERIVATIVES

Since manganese carbonyl derivatives have been relatively little studied, it is still early to speak of their widespread application. However, several prospects already exist for making use of these compounds.

During 1956–1957 the first papers appeared[211–214] on the use of methylcyclopentadienylmanganese tricarbonyl and its derivatives as anti-knock compounds. A great deal of work is now being done on the industrial application of cyclopentadienylmanganese tricarbonyl, which is almost twice as effective as tetraethyl-lead, at present widely employed for this purpose; furthermore, it is considerably less toxic[215]. Information is available[216,217] on the use for anti-knock purposes of other derivatives of manganese carbonyl, not containing a cyclopentadienyl ring, including decacarbonyldimanganese itself.

Derivatives of manganese carbonyl find some application as additives to lubricating oils[218].

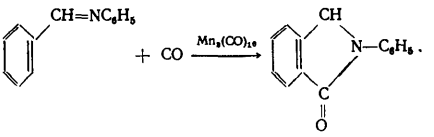
Furthermore, various compounds containing an M–CO bond are gradually finding increasingly wide use as catalysts for various processes. More than fifty types of reactions catalysed by metal carbonyls are known at the present time[199,219], many of them involving manganese carbonyl. The most important of these processes are given below.

(a) Carbonylation of Organic Compounds

Manganese carbonyl and its derivatives can act as a source of carbonyl groups for various processes of carbonylation. For example, dimethylformamide is formed by reaction between decacarbonyldimanganese and excess of dimethylamine[219,220]:

$$22\,(CH_3)_2NH + 3Mn_2(CO)_{10} \rightarrow 2\{Mn[(CH_3)_2NH]_6\}[Mn(CO)_5]_2 + 10HCON(CH_3)_2 .$$

Transfer of carbon monoxide can occur also catalytically in the presence of manganese carbonyl heated to 200–250°C under a high pressure of carbon monoxide. An example of such transfer is the carbonylation of *N*-phenylbenzylideneimine[221]:



Derivatives of metal carbonyls can be used to carbonylate other organic compounds besides amines, e.g. alkyl halides[222,223]:

$$CH_3Cl + NaMn(CO)_5 \rightarrow CH_3{-}Mn(CH)_5 \xrightarrow{CO} CH_3CO{-}Mn(CO)_5 \xrightarrow{Br_2} CH_3COBr + BrMn(CO)_5$$

(b) Hydrogenation

Various organic compounds can be hydrogenated in the presence of a hydrogen carbonylmanganate. With proton-acceptors present, hydrogen pentacarbonylmanganate decomposes forming decacarbonyldimanganese, while the hydrogen atom liberated is transferred to the acceptor:

$$2HMn(CO)_5 \rightarrow 2H^{\cdot} + Mn_2(CO)_{10}$$

$$CH_3COCH_3 + 2H^{\cdot} \rightarrow CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 .$$

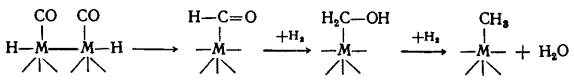
At elevated temperatures the hydrogenation may be autocatalytic[223,224].

(c) Transfer of Carbon Monoxide and Hydrogen (Fischer–Tropsch Synthesis)

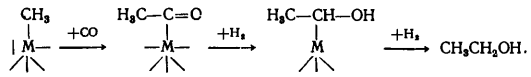
An example of the simultaneous transfer of carbon monoxide and hydrogen is provided by the synthesis of ethanol from methanol, carbon monoxide, and hydrogen in the presence of manganese carbonyl[225,226]:

$$CH_3OH + CO + H_2 \xrightarrow{Mn_2(CO)_{10}} CH_3CH_2OH .$$

The mechanism of this reaction can be represented by a scheme comprising (i) formation of methyl from carbon monoxide and hydrogen



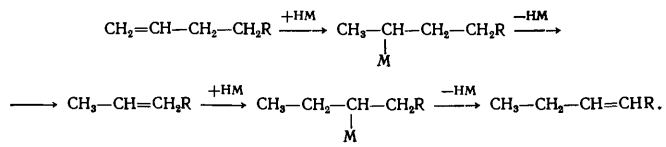
and (ii) chain growth



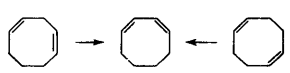
This reaction will probably provide a method of obtaining higher alcohols.

(*d*) Isomerisation of Alkenes

The isomerisation of alkenes involves the intermediate addition of the hydrocarbonylmetal complex (HM) at the double bond in the organic molecule, followed by its elimination according to the scheme



Wittenberg and Seibt[227] accomplished the isomerisation of cyclo-octa-1,4(and 1,5)-diene into cyclo-octa-1,3-diene in the presence of decacarbonyldimanganese:



(*e*) Polymerisation of Alkenes

Little work has yet been done on the possibility of using metal carbonyls as catalysts for the polymerisation of unsaturated compounds. Bamford and his coworkers[228,229] have accomplished the polymerisation of methyl methacrylate in the presence of manganese and rhenium carbonyls in polar solvents, and found them to exert a stereoregulating effect on processes of radical polymerisation.

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γ- and δ-Unsaturated δ-Lactones

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CONTENTS

I. Introduction 198
II. Synthesis of unsaturated δ-lactones 198
1. Dehydration of δ-keto-acids to unsaturated δ-lactones 198
2. Other syntheses of unsaturated δ-lactones 200
III. Reactions of unsaturated δ-lactones 201
1. Hydrolysis, alcoholysis, and ammonolysis 201
2. Reduction with lithium tetrahydroaluminate 202
3. Reaction with organomagnesium compounds 202
4. Isomerisation of unsaturated δ-lactones in the presence of sodium alkoxides 204
5. Catalytic hydrogenation of unsaturated δ-lactones 204
6. Halogenation of unsaturated δ-lactones 204
7. Reactions of the α-methylene group 205
8. Photolysis of unsaturated δ-lactones 205

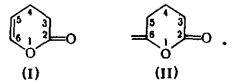
I. INTRODUCTION

Many substances containing unsaturated γ- and δ-lactone rings exhibit physiological activity. It is sufficient to mention the aglycones of cardiac poisons of vegetable and animal origin, various coumarin derivatives, and lactones of the santonin group to have an idea of the importance of compounds of this type.

The varied physiological action of these substances (anthelmintic, effect on heart muscle, ability to arrest the growth of animal tissues and plants), and also the antibiotic activity of the simpler lactones (protoanemonin, parasorbic acid, kawain), are associated with the presence in these compounds of unsaturated lactone rings[1].

These facts are attracting chemists to the study of unsaturated lactones. From the point of view of reactivity, the greatest interest attaches to those in which the double bond is in the vinyl position—either in the ring or outside it—with respect to the heteroatom, this position being responsible for their peculiar chemical behaviour.

Whereas the chemistry of the five-membered unsaturated lactones (but-3(or 4)-en-4-olides) has been developed for many years[2], the principal branches of the chemistry of the six-membered unsaturated lactones (pent-4(or 5)-en-5-olides) have been studied only during the past decade. These investigations have shown wide opportunities for the use of unsaturated δ-lactones in organic synthesis, and have revealed a difference in behaviour between the two types of unsaturated δ-lactones, differing in the position of the double bond—3,4-dihydro-2-pyrones (I) and 6-alkylidenetetrahydro-2-pyrones (II).



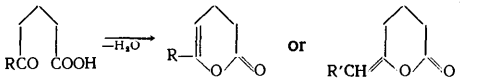
(I) (II)

The present review represents the first attempt to summarise and systematise information on the chemistry of the unsaturated δ-lactones published up to 1966 inclusive.

II. SYNTHESIS OF UNSATURATED δ-LACTONES

1. Dehydration of δ-Keto-acids to Unsaturated δ-Lactones

The chief method of obtaining unsaturated δ-lactones is the cyclodehydration of δ-keto-acids, which can occur in different ways:

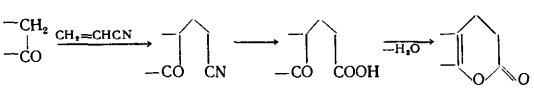


where R = R'CH_2.

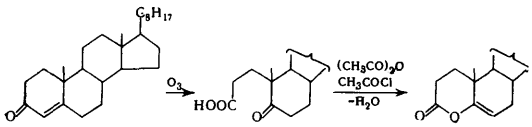
In isolated cases water is eliminated from δ-keto-acids when they are distilled or heated (thermal enol-lactonisation). Since the reaction occurs at a relatively high temperature, this method is used to obtain unsaturated lactones only from keto-acids boiling above 200–250°C.[3-6]

The most important and widely used procedure for the enol-lactonisation of δ-keto-acids† is their dehydration in the presence of acetic anhydride alone[13-23], mixed with acetyl chloride[24,25], or with the addition of catalytic quantities of sodium acetate[26,27], sulphuric acid[6], or perchloric acid[28-30]. This route has been used to prepare δ-lactones having the double bond in the ring (3,4-dihydro-2-pyrones)[30-37] or in the exocyclic position (6-alkylidenetetrahydro-2-pyrones)[4,38,39].

† The possibility of preparing unsaturated δ-lactones in this way is determined mainly by the accessibility of the initial δ-keto-acids, which in turn are synthesised in various ways. Among published general methods of obtaining δ-keto-acids[7-12] the most convenient is the hydrolysis of δ-keto-nitriles[12], which result from the addition of acrylonitrile to ketones. Using this method of synthesising δ-keto-acids, we can pass from ketones to unsaturated δ-lactones in three stages:

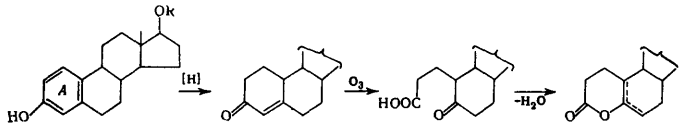


The dehydration of δ-keto-acids is widely used for the preparation of steroid unsaturated δ-lactones. For this purpose the natural steroids are converted by ozonolysis into the δ-keto-acids, which are then lactonised by one of the above methods[25,26]; for example

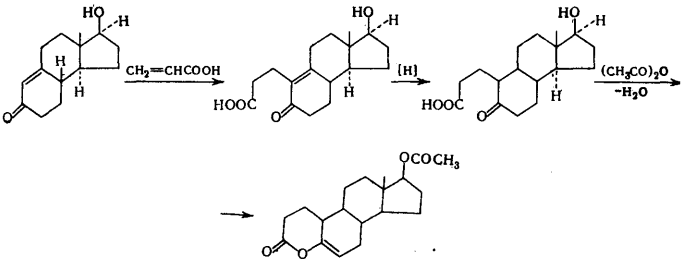


From cholestenone[40-43], testosterone[40,44,45], progesterone[46-49], androsterone and its derivatives[50-52], and cortisone[47,53] have been obtained the corresponding 4-oxasteroids in order to study the physiological action of these lactones, and also to obtain labelled androgens and corticosteroids (see Section III, 3).

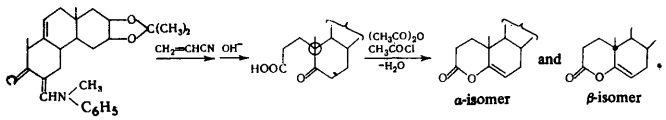
Unsaturated δ-lactones have been obtained also from oestrogens‡, the first stage of the process being in this case reduction of the phenolic ring A to the corresponding unsaturated ketone[54]:



where R = $COCH_3$, COC_6H_5. One of these lactones (with R = $COCH_3$) has been obtained synthetically[55] and then used for the synthesis of 19-nortestosterone:

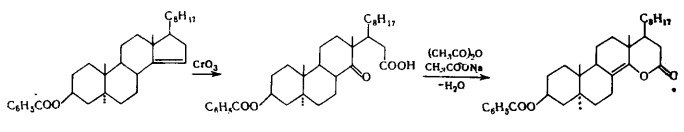


The lactonisation of δ-keto-acids was used by Woodward et al.[26] to prepare tetracyclic unsaturated δ-lactones, which were employed in one of the stages of their total synthesis of steroids:



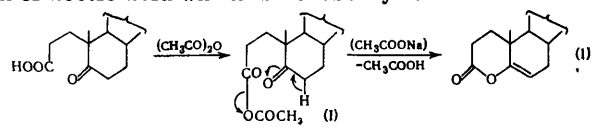
By varying the sequence in which the individual stages in this scheme were accomplished, it then proved possible to obtain predominantly the β-isomer[56-58] (corresponding to the configuration of natural steroids), which, according to Woodward, is obtained in only 13% yield.

In order to obtain a steroid unsaturated δ-lactone in which the D-ring was lactonic, use was made of the δ-keto-acid formed by the oxidation of cholest-14-en-3β-yl benzoate[59]:



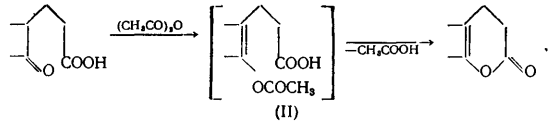
‡ In contrast to the examples given above, the absence of an angular methyl group in position 10 suggests that both isomeric lactones, differing in the position of the double bond, will be formed.

It may be concluded from published data on the mechanism of the action of acetic anhydride in the lactonisation of δ-keto-acids that acylation products are formed initially. But according to Woodward[26] acetic anhydride acylates the carboxyl of the δ-keto-acid to form a mixed anhydride (I)§, from which the unsaturated δ-lactone is obtained by subsequent intramolecular enolacylation of the carbonyl group; the sodium acetate catalyses the elimination of acetic acid which is necessary for this reaction:



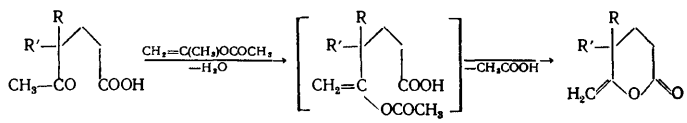
This view of the role of acetic acid is supported by results obtained by Rosenthal et al.[60], who also isolated a mixed anhydride by the action of acetic anhydride on a triterpenoid δ-keto-acid.

However, it may be postulated that the acetic anhydride reacts in a different manner—that it acylates the δ-keto-acid at the carbonyl group with formation of the acetate of the enolic form¶ of the δ-keto-acid (II), subsequent intramolecular reacylation[63,64] of which yields the unsaturated δ-lactone:



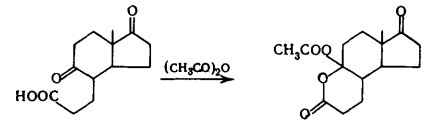
In this case the role of substances of the acidic and basic character of sodium acetate[26], acetyl chloride[25], and sulphuric acid[6], which are used as catalytic additions in enol-lactonisation by means of acetic anhydride, is to facilitate enolisation of the carbonyl group, which is necessary for the reaction to occur in this way. Several authors use scheme (2) to explain the role of acetic anhydride in the lactonisation of δ-keto-acids[65-67].

Scheme (2) also provides an explanation of the anomalous behaviour of γγ-disubstituted δ-keto-acids, which remains unaffected by boiling acetic anhydride[68,69], but are converted into the corresponding unsaturated lactones in 81-99% yield on treatment with isopropenyl acetate:



where R = R′ = CH_3, C_6H_5; R = C_6H_5 and R′ = o-$ClC_6H_4CH_2$. The enolisation of keto-acids containing no γ-hydrogen atom should be difficult, since it can occur only by means of the methyl hydrogen atoms. Therefore the formation of unsaturated acetates of the type (II), which are required

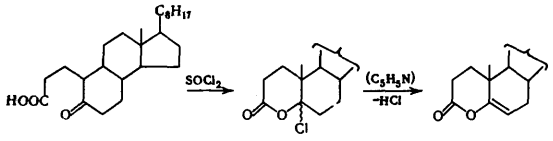
§ On the basis of the infrared spectra Woodward assumed an open-chain structure for the intermediate anhydride (I). More recently, however, it has been shown (from the infrared and nuclear magnetic resonance spectra) that an anhydride of this type obtained from a bicyclic keto-acid has a cyclic structure[27]:



¶ Acetates of the enolic forms of ketones are known to be obtained by the action of acetic anhydride on ketones in the presence of sodium acetate or sulphuric acid[61,62].

for the subsequent production of unsaturated lactones, will take place only in the presence of such a strong acylating reagent as isopropenyl acetate.

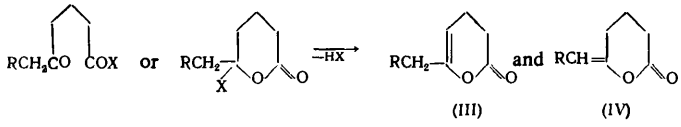
Acid chlorides (acetyl[7,70,71], oxalyl[24], and thionyl[24,72,73]) are widely used for the lactonisation of δ-keto-acids, being more effective than acetic anhydride or phosphorus pentachloride[74]. In this case lactonisation probably involves intermediate formation of the chlorides of the keto-acids, which, as has recently been demonstrated spectroscopically, have (unlike the δ-keto-acids themselves[75]), a cyclic structure[9,76], and readily split off hydrogen chloride[25,45] to form the unsaturated δ-lactones; e.g. [25]



In individual cases these intermediate cyclic acid chlorides have been isolated[9,25,45,54,76-78]. Their properties, which differ from those of ordinary chlorides of carboxylic acids, also confirm their cyclic structure[25,78].

Thus the lactonisation of δ-keto-acids can be accomplished either by their direct dehydration (thermal enol-lactonisation) or by the intermediate conversion of the original acids into acylation products (action of acetic anhydride) or cyclic acid chlorides (action of acid chlorides).

When hydrogen atoms are present in the γ- and ε-positions of δ-keto-acids and their derivatives†, isomeric unsaturated δ-lactones can be obtained, with the double bond either in the ring (III) or in the exocyclic position (IV):



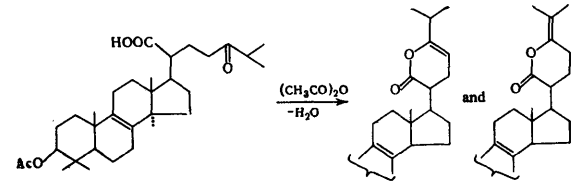
(III) (IV)

where X = Cl, CH_3COO, OH. Which of the isomeric lactones (III) and (IV) is obtained in each individual case is determined either by the direction in which the initial keto-acid undergoes enolisation or by the direction in which HX is eliminated from their cyclic forms[79-83].

Spectral methods have been successfully employed for the investigation of these unsaturated δ-lactones‡. It has been shown that the stretching vibrations of an exocyclic double bond are represented in the infrared spectra of the unsaturated δ-lactones by intense absorption at 1649–1662 cm^{-1},[84,85] whereas the stretching vibrations of an endocyclic double bond in these compounds correspond to extremely weak bands in the range 1695–1710 cm^{-1}.[54,84]

The Raman spectra can also be successfully used to establish the position of the double bond in unsaturated δ-lactones, since they show a difference of the same order as in the infrared spectra for lactones having semicyclic and endocyclic double bonds. However, the intensity of absorption in the region of the carbon–carbon double bond is extremely strong in the Raman spectra for both types of lactones[84].

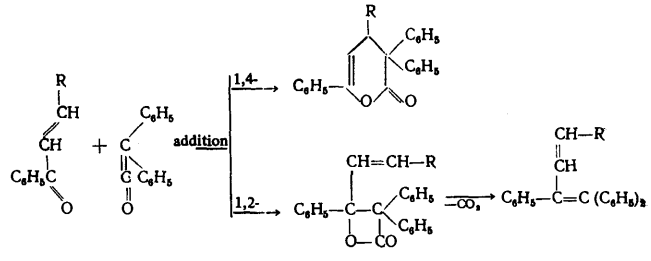
The application of spectral methods of investigation has shown that the simplest δ-keto-acids, whose structure permits the formation from them of both types of unsaturated lactones, are converted predominantly into those containing an endocyclic (more substituted) double bond[84]. Recently, however, examples have been described of the lactonisation of δ-keto-acids of complicated polycyclic structure with the formation of both possible isomers[54,60,91]. Thus the δ-keto-acid obtained by ozonolysis of the triterpenoid eburicoic acid is dehydrated to a mixture of isomeric lactones, the different positions of the double bond in which have been proved by ozonolysis and by the nuclear magnetic resonance spectra[60,91]:



The nuclear magnetic resonance spectra have been used to establish the position of the double bond in other polycyclic unsaturated δ-lactones[5,16,27,60,91,92].

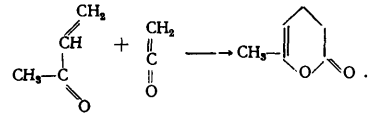
2. Other Syntheses of Unsaturated δ-Lactones

Unsaturated δ-lactones can be synthesised (in 20–30% yield) by Staudinger's method[93]—from ketens and αβ-unsaturated ketones (1,4-addition)—when diene hydrocarbons are also formed, by decarboxylation of the β-lactones produced by 1,2-addition:

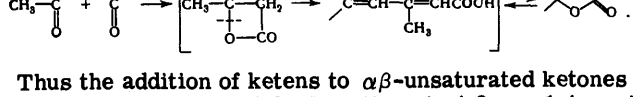


where R = C_6H_5, p-$CH_3OC_6H_4$, p-$(CH_3)_2NC_6H_4$.

The reaction between but-3-en-2-one and keten (the first members of each series) yields only the 1,4-addition product[94]:



Alk-3-en-2-ones react with keten only in the presence of a catalyst (boron trifluoride), forming unsaturated δ-lactones in which the double bond is in the βγ-position. Production of the latter is explained by isomerisation of the β-lactones formed initially by 1,2-addition; e.g.[95]

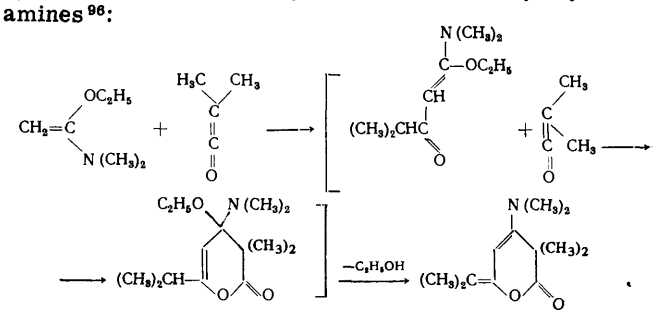


Thus the addition of ketens to αβ-unsaturated ketones takes place in both possible directions in 1,2- or 1,4-positions depending on the structure of both components.

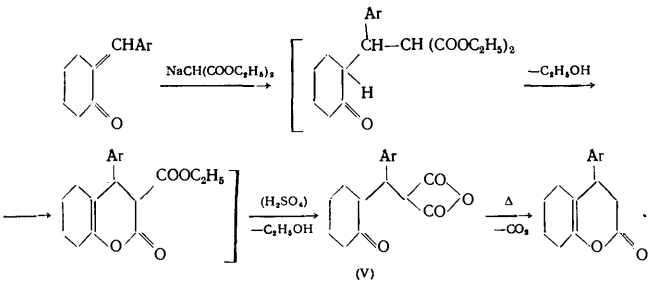
† In contrast to the acid chlorides[25] and anhydrides[27] the δ-keto-acids themselves exist in the open-chain form[75]. However, this fact does not exclude the possibility of their reacting in their cyclic form during lactonisation.

‡ The infrared and Raman spectra of these unsaturated δ-lactones exhibit an intense carbonyl absorption in the range 1750–1780 cm^{-1},[84,85,87,88] which distinguishes them from unsaturated δ-lactones in which the double bond is in the αβ- or βγ-position (carbonyl absorption at 1710–1730 cm^{-1}) and from 2-pyrones (1720–1740 cm^{-1}).[86,89,90]

δ-Lactones containing an exocyclic double bond can be synthesised from dimethylketens§ and 1-alkoxyvinylamines[96]:

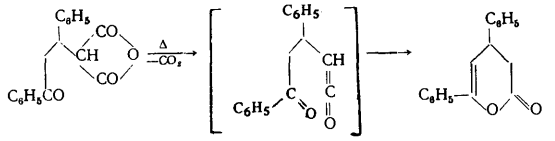


The condensation of benzylidene- and *p*-methoxybenzylidene-cyclohexanone with sodiomalonic ester (the Michael reaction)[98] yielded unsaturated α-ethoxycarbonyl-δ-lactones, which were easily further converted into substituted γ-keto-malonic anhydrides, the latter again being cyclised (on heating) into unsaturated δ-lactones:

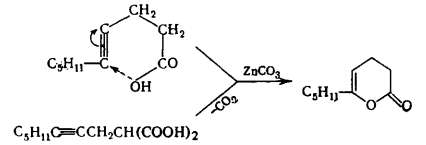


(V)

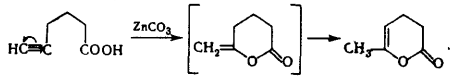
A similar conversion of γ-keto-malonic anhydrides (V)¶ into unsaturated δ-lactones was observed by Mannich and Butz[17], who regarded this reaction as an intramolecular enolacylation of an anhydride keto-group. It may be supposed, however, that under these conditions acylation will be effected by ketens formed as intermediates†, which, according to Staudinger's results[99], are readily obtained from such malonic anhydrides on heating; e.g.



Unsaturated δ-lactones are formed also by the cyclisation of pent-4-ynoic acid or the corresponding prop-2-ynylmalonic acids under the influence of zinc carbonate[100]; e.g.

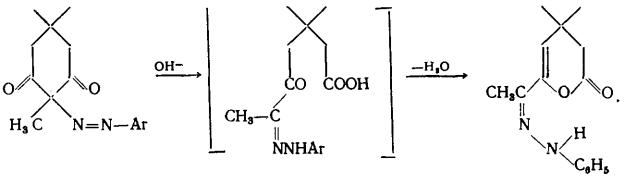


Under these conditions hex-5-ynoic acid could be expected to yield a δ-lactone containing an exocyclic double bond. However, the double bond migrated into the ring, and 3,4-dihydro-6-methyl-2-pyrone was obtained:

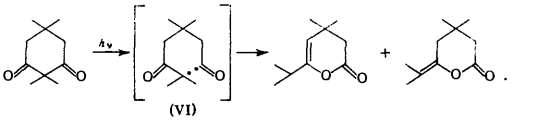


In spite of the comparatively good yields (45–65%) of unsaturated δ-lactones, application of this method is restricted by the relative inaccessibility of the initial alkynoic acids.

Unsaturated δ-lactone rings are formed by the alkaline hydrolysis of azo-derivatives of cyclohexane-1,3-diones (obtained by the Japp–Klingemann method); e.g.[101]



The photoisomerisation has recently been described of 2,2,5,5-tetramethylcyclohexane-1,3-dione (on exposure of a benzene solution) into a mixture of δ-lactones containing an exocyclic or an endocyclic double bond (in 92% and 1.3% yield respectively)[102]:



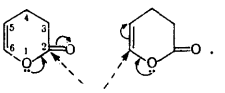
(VI)

This interesting reaction probably involves the intermediate formation of a diradical (VI), which then cyclises into an unsaturated lactone.

III. REACTIONS OF UNSATURATED δ-LACTONES

Unsaturated δ-lactones are highly reactive; in many respects their activity is similar to that of vinyl esters—of which they are cyclic analogues—and of unsaturated γ-lactones[2].

Like these compounds, unsaturated δ-lactones react readily with nucleophilic reagents. Since the distribution of electron density in the unsaturated lactones is such that the ring carbon atoms 2 and 6 are positively charged, it can be expected that attack by nucleophilic reagents will take place at one of these carbon atoms, with subsequent cleavage of the 1–2 or the 1–6 bond and formation of two series of derivatives (as occurs with 2-pyrones)[97]:



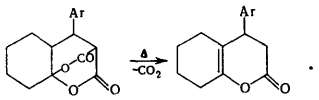
Unsaturated δ-lactones react readily also with electrophilic reagents, forming products of addition at the double bond, which possesses enhanced nucleophilic character in unsaturated lactones (as also in vinyl ethers).

1. Hydrolysis, Alcoholysis, and Ammonolysis

Unsaturated δ-lactones react readily‡ with water, the

§ Use of keten itself in this reaction[97] yields 2-pyrones.

¶ These substances may have the structure of the isomeric dilactones[98], which on decarboxylation also give the corresponding δ-lactones:

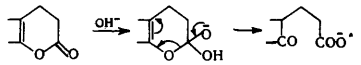


† The formation of these ketens (not the unsaturated lactones) was expected by Mannich and Butz[17], when investigating the behaviour of malonic anhydrides on heating.

‡ Some hydrolysis of unsaturated δ-lactones occurs even under the influence of atmospheric moisture[30,103].

lactone ring being opened and δ-keto-acids being formed.

Alkaline hydrolysis takes place still more easily, and leads (often in the cold) to the formation of quantitative yields of salts of the δ-keto-acids:

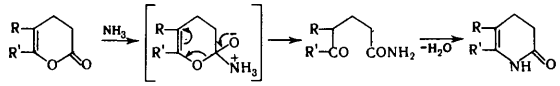


However, the ease of ring opening on alkaline hydrolysis may vary greatly with the nature and position of substituents in the unsaturated δ-lactone and with the strength of the base employed[13,15,17,49,93].

Acid hydrolysis has been described only in the case of one unsaturated lactone, which contained a 4-amino-group[96].

The reaction between unsaturated δ-lactones and alcohols, which results in the formation of esters of δ-keto-acids, also requires the presence of alkaline or acidic catalysts (in the absence of a catalyst the reaction goes very slowly on prolonged heating[17]). The ease of alcoholysis in the presence of acids is, perhaps, explained by protonation of the double bond in the lactone, resembling what occurs in the alcoholysis of vinyl esters[104]. This reaction is used for the preparation of esters of δ-keto-acids[4,31,34,35,68,105].

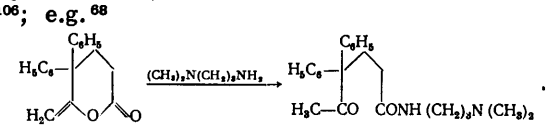
The action of ammonia on unsaturated δ-lactones leads to opening of the ring at the 1–2 bond§ with the formation of δ-keto-amides. Depending on their structure, the latter can be dehydrated with varying ease into the corresponding 5,6-unsaturated lactams (the nitrogen analogues of the δ-lactones)[3,13,17,34,35,38,93,106–108]; e.g.[107]



where R = C_2H_5 and R′ = C_6H_5.

The conversion of steroid unsaturated δ-lactones into the corresponding unsaturated δ-lactams (by the action of ammonia) provided a new method for the synthesis of azasteroids[51,109–111].

With amines unsaturated δ-lactones give high yields (usually in the cold) of substituted δ-keto-amides[13,17,68–74,103,106]; e.g.[68]



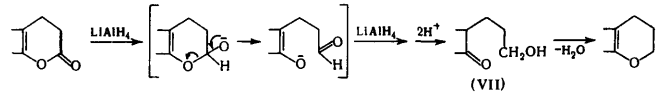
These examples show that unsaturated δ-lactones react with water, alcohols, ammonia, and amines under far milder conditions than do saturated δ-lactones. The reactions of hydrolysis, ammonolysis, and alcoholysis, resulting in the formation of δ-keto-acids and their derivatives, are used for the identification of unsaturated δ-lactones.

2. Reduction with Lithium Tetrahydroaluminate

Recent investigation of the reactions undergone by unsaturated δ-lactones with lithium tetrahydroaluminate has shown that various reduction products are formed depending on the position of the double bond.

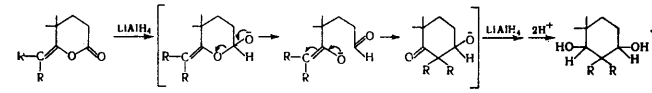
§ Addition at the 1-6 bond should have resulted in the formation of δ-amino-acids, but the latter were not observed in these cases.

Unsaturated δ-lactones containing a cyclic double bond (3,4-dihydro-2-pyrones) are reduced to 5-hydroxyalkanones (VII), which on dehydration readily undergo cyclisation to dihydropyrans[112]:



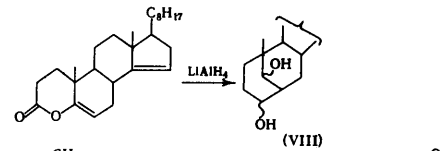
(VII)

Unsaturated δ-lactones containing an exocyclic double bond (6-alkylidenetetrahydro-2-pyrones) are reduced by lithium tetrahydroaluminate to cyclohexane-1,3-diols (in 52–65% yield), with rearrangement[113]:

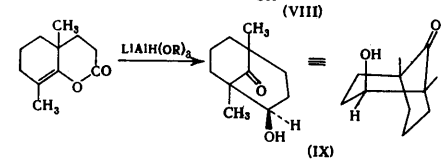


where R = H, CH_3.

The reduction of δ-lactones whose exocyclic double bond forms part of a ring fused with the lactone ring yields bridged compounds. Thus 4-oxacholest-5-en-3-one is converted under the influence of lithium tetrahydroaluminate into the bridged diol (VIII)¶ [114], whereas the action of lithium hydrotri-t-butoxyaluminate on a bicyclic lactone of similar structure yields an incompletely reduced product, the hydroxy-ketone (IX)[115]:



(VIII)



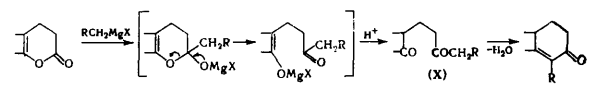
(IX)

Martin et al.[116] have shown that in the last example the reaction goes stereospecifically with formation of the epimer having the hydroxyl in the axial position (IX).

3. Reaction with Organomagnesium Compounds

δ-Lactones which differ in the position of a double bond behave differently with organomagnesium compounds.

3,4-Dihydro-2-pyrones (lactones having the double bond in the ring) add one or two moles of Grignard reagent depending on the conditions. When the reactants are added in the reverse order in the proportions 1 : 1 at −20°C, one mole of the organomagnesium compound is added. The reaction products are 1,5-diketones (X), which are further converted by intramolecular aldol condensation into cyclohex-2-enones[117]:

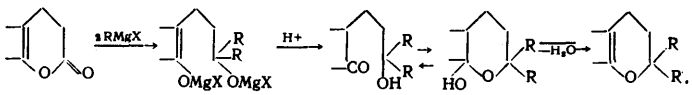


(X)

With excess of the organomagnesium compound at temperatures above 0°C, two moles thereof are added, the

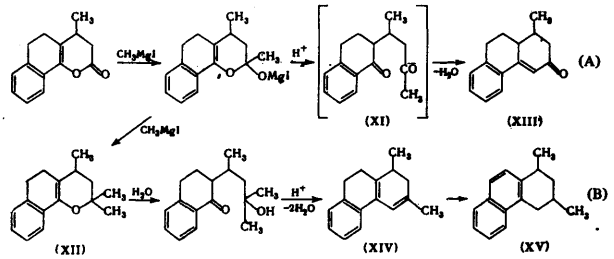
¶ The product of the reduction of this lactone by lithium tetrahydroaluminate had earlier been erroneously attributed the structure 3,5-seco-cholestane-3,5-diol[43].

main reaction products[118] being 3,4-dihydropyrans (yield 47–80%):

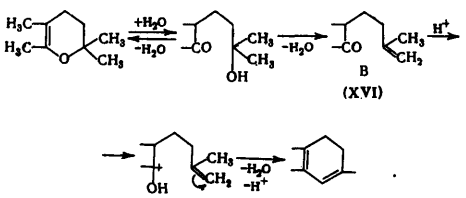


The reaction can be utilised for the preparation of substituted dihydropyrans.

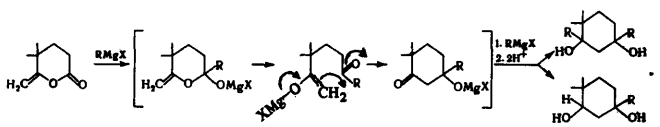
Similar observations were made by Belleau[24]. However, the reaction products formed initially—the diketone (XI) and the dihydropyran (XII)—were converted under the conditions of hydrolysis into respectively the unsaturated ketone (XIII) and the cyclohexadiene hydrocarbon (XIV), the latter of which immediately isomerised into the hydrocarbon (XV). These changes were explained by the scheme



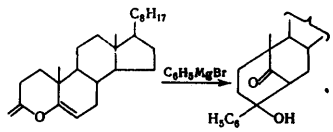
Formation of cyclohexadiene hydrocarbons by the hydrolysis of substituted dihydropyrans has been observed by the present reviewers[119], who showed that, contrary to Belleau's scheme, these hydrocarbons were formed as a consequence of intramolecular cyclisation of δε-unsaturated ketones (XVI) formed from the dihydropyrans; e.g.



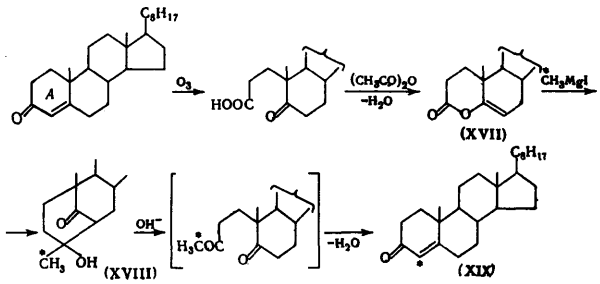
The action of organomagnesium compounds of δ-lactones containing an exocyclic double bond results in the formation of cyclohexane-1,3-diols[120], whose appearance is explained by a rearrangement resembling that described above in the reduction of unsaturated lactones with lithium tetrahydroaluminate; e.g.



Rearrangement accompanies also† the reaction of organomagnesium compounds with steroid δ-lactones containing an exocyclic (with respect to the lactone ring) double bond. In this case the reactions terminate at the stage of formation of bridged hydroxy-ketones[123,124] (reaction products of this type had earlier been regarded erroneously as 1,5-diketones and hemiacetals[40,41]); for example



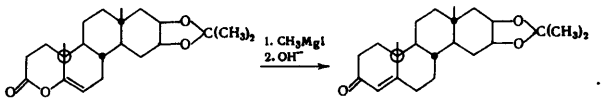
The interaction of organomagnesium compounds with steroid unsaturated lactones has been described in many papers. Thus Fujimoto[40] used this reaction to develop a method for introducing labelled carbon into position 4 in ring A of testosterone and cholestenone. The action of methylmagnesium iodide on the unsaturated lactone (XVII) (obtained from natural cholestenone) produces a bridged hydroxy-ketone (XVIII), which is then converted (by treatment with alkali) into cholestenone (XIX), which is identical with the natural product[40]:



It is obviously possible by means of this series of reactions to break down and recreate ring A of the steroid. In this way, with the use of methylmagnesium iodide containing labelled carbon, the latter can be introduced into position 4 of ring A. This scheme of Fujimoto's served (without isolation of the intermediate hydroxy-ketone of type (XVIII) for the preparation of many ^{14}C-labelled steroids for the study of their metabolism. Cholestenone[41], progesterone[46,47], and 17-hydroxy-17α-methylandrost-4-en-3-one[51] have been obtained in this way.

Fujimoto's scheme can be used also to introduce an alkyl group into the 4-position of the steroid ring system by bringing other alkylmagnesium halides into reaction with steroid unsaturated lactones. Various 4-methylated steroids—4-methylcholestenone[42,125,126], 17-hydroxy-4-methylandrost-4-en-3-one[44,125,126], 17-hydroxy-4-methyl-19-norandrost-4-en-3-one[126], and also 4-ethyl-17-hydroxyandrost-4-en-3-one[126]—have thus been prepared with the aim of studying their androgenic activity. The acetates of 17-hydroxy-4-methyl-19-norandrost-4-en-3-one[54,92] and 4-methylhydrocortisone[127] have been synthesised in a similar manner.

The reaction between unsaturated lactones and organomagnesium compounds was used by Woodward[26] to build up the ring A in his total synthesis of steroids:



The stereospecificity which he observed in the Grignard reaction with lactones differing in configuration at $C_{(10)}$ served for the separation of α- and β-epimers and confirmed their configuration[56,57,128].

Thus the reaction between unsaturated δ-lactones containing an exocyclic (relative to the lactone ring) double bond and organomagnesium compounds has been widely

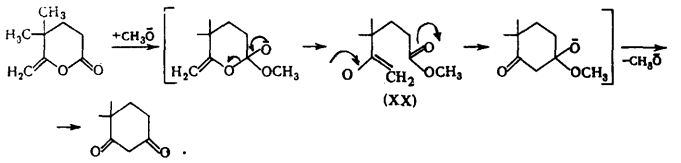
† It was found that rearrangement also accompanied reaction of the linear analogues of unsaturated δ-lactones—vinyl esters—with organomagnesium compounds[121]. The acetate of the enolic form of cyclohexanone, however, reacts normally[122].

used for various synthetic purposes—to prepare cyclohexane-1,3-diols, for the synthesis of 4-methylated steriods containing labelled carbon, and also in the complete synthesis of steroids.

4. Isomerisation of Unsaturated δ-Lactones in the Presence of Sodium Alkoxides

When heated with sodium ethoxide (for 2–10 h), unsaturated δ-lactones isomerise‡ into cyclohexane-1,3-diones[129,130].

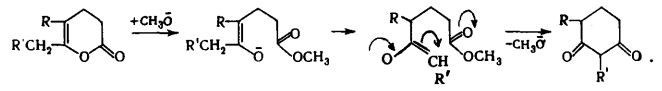
With unsaturated δ-lactones containing an exocyclic double bond (e.g. tetrahydro-5,5-dimethyl-6-methylene-2-pyrone) this transformation is explained by the scheme



(XX)

The anion (XX) is then cyclised by a kind of intramolecular Claisen condensation and is converted into the corresponding cyclohexane-1,3-dione.

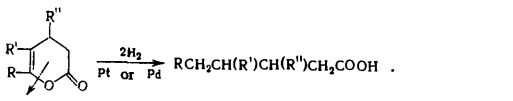
Lactones containing an endocyclic double bond are also converted, when heated with sodium methoxide, into the corresponding cyclohexane-1,3-diones. In this case the double bond probably migrates from the γδ- to the δε-position[130]:



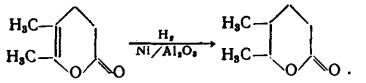
The isomerisation of unsaturated δ-lactones in the presence of sodium methoxide can be utilised for the preparation of cyclohexane-1,3-diones.

5. Catalytic Hydrogenation of Unsaturated δ-Lactones

In the presence of catalysts one or two molecules of hydrogen can be added to unsaturated δ-lactones, with the formation respectively of saturated lactones and saturated acids. Lactones containing a double bond in the ring are hydrogenated in the cold§ over platinum or palladium with the formation solely of carboxylic acids[30,131,132]:

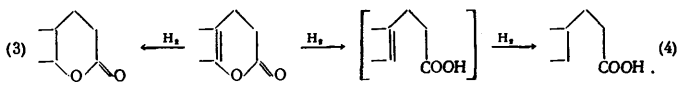


This hydrogenolysis is the only example of the opening of the unsaturated δ-lactone ring at the 1–6 bond. The hydrogenation of lactones of this type over nickel on aluminium oxide in a flow system at 200°C led to the formation of a saturated lactone¶; for example[31]

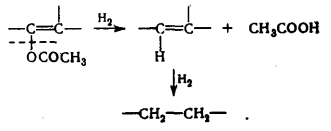


Lactones containing an exocyclic double bond are hydrogenated over a platinum catalyst (in the cold) in both possible ways[25,31].

Thus the hydrogenation of unsaturated δ-lactones can occur simultaneously in two ways—at the double bond with formation of a saturated lactone (3) and at the 1–6 bond of the lactone ring with subsequent hydrogenation of the resulting unsaturated acid (4)—the relative rates of these reactions, determined by the structure of the δ-lactone and the conditions of hydrogenation, governing the formation of the final reaction products:



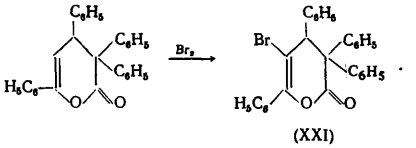
It is interesting that hydrogenation of the linear analogues of the unsaturated lactones—enolic acetates—probably occurs in the second way (hydrogenolysis of the ester bond followed by hydrogenation of the double bond)[137]:



6. Halogenation of Unsaturated δ-Lactones

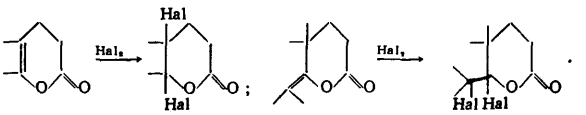
The properties of the double bond in unsaturated δ-lactones, which by analogy with vinyl esters should possess enhanced nucleophilic character, have been studied only with respect to halogenation. The lactone ring is preserved during these reactions.

Staudinger[93] brominated 3,4-dihydro-3,3,4,6-tetraphenyl-2-pyrone, obtaining a monobromo-derivative to which he attributed without proof the structure of a brominated unsaturated lactone (XXI):



(XXI)

A detailed study of the halogenation of unsaturated δ-lactones was made by Levina, Shusherina, and their collaborators[138–141], who showed that in the cold bromine[138,142] or chlorine[141] (by the action of sulphuryl chloride†) is readily added at the double bond to form reactive dihalides:



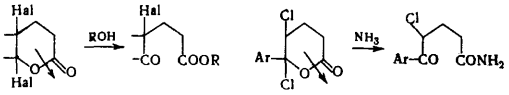
‡ Brief action of sodium ethoxide (in the cold) on unsaturated δ-lactones followed by treatment with water yields esters of δ-keto-acids[53].

§ Unsaturated δ-lactones containing the double bond in the αβ- or βγ-position add hydrogen only at the double bond under the same conditions[95,133]. Endeavours have been made to utilise this difference in behaviour between lactones containing the double bond in different positions to establish the structure of naturally occurring compounds containing an unsaturated lactone ring[134,135].

¶ An attempt to explain the formation of saturated acids by hydrogenolysis of initially formed saturated lactones[131] proved to be untenable[136].

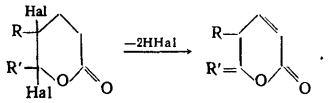
† The action of chlorine on unsaturated δ-lactones involves not only addition at the double bond but also replacement of hydrogen.

The dihalides react with water, alcohols[142-145], and ammonia[146] with opening of the lactone ring and formation of γ- and ϵ-halogenated δ-keto-acids, their esters, and their amides (in 70–100% yield):



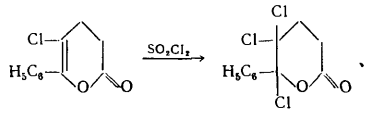
where Hal = Cl, Br and R = H, Alk.

On distillation dihalogenolactones, as well as the trihalogenolactones obtained from them by further halogenation, undergo partial[148] or complete[138,139] dehydrohalogenation, during which the lactone ring is preserved:

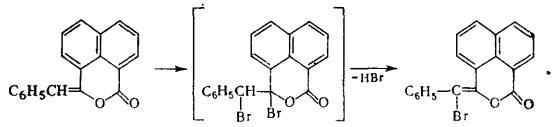


These reactions of the indirect dehydrogenation‡ of unsaturated δ-lactones (involving stages of halogenation and subsequent dehydrohalogenation) provide convenient routes for obtaining difficultly accessible 2-pyrones of various structures[138-141,147-149], including those containing a 5-bromo-substituent or a 6-bromomethyl group.

It is interesting that the nucleophilic character of the double bond is diminished in 5-chloro-3,4-dihydro-2-pyrones. They do not react at all with bromine in the cold, though they add chlorine at the double bond[150]:

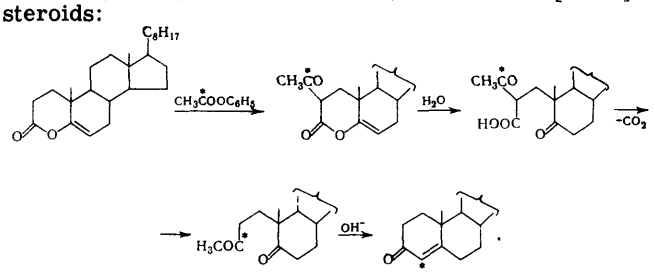


A brominated lactone containing an exocyclic double bond was obtained by the bromination of 3-benzylidenenaphthalide[151]:



7. Reactions of the α-Methylene Group

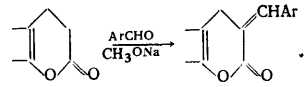
In the presence of sodium hydride the steroid unsaturated δ-lactones obtained from cholestenone and testosterone react as the methylene component in the aldol condensation with phenyl acetate[25]. When labelled phenyl acetate was used, the resulting acylated unsaturated lactones were converted (through the stages of hydrolysis, decarboxylation, and condensation) into labelled [4-^{14}C] steroids:



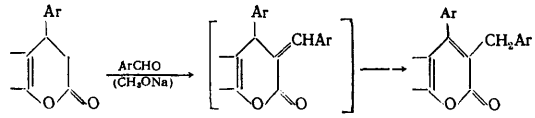
‡ The direct dehydrogenation of unsaturated δ-lactones to 2-pyrones—in boiling cymene over palladium on carbon—has been described only in the case of a triterpenoid unsaturated lactone[60].

This route has been used also to obtain labelled progesterone[49].

Unsaturated δ-lactones condense with aromatic aldehydes in the presence of sodium methoxide[152] to form 3-benzylidene-3,4-dihydro-2-pyrones:

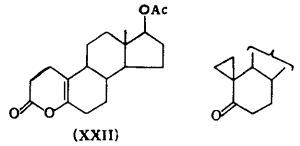


2-Pyrones can be obtained by means of this reaction from unsaturated lactones containing a 4-aryl substituent, since the benzylidene derivatives formed as intermediates immediately isomerise into 3-benzyl-2-pyrones:



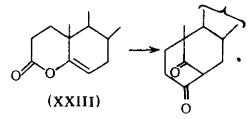
8. Photolysis of Unsaturated δ-Lactones

Interesting results have been obtained by the ultraviolet irradiation of unsaturated δ-lactones. The steroid δ-lactones (XXII) containing an endocyclic double bond was converted under these conditions into the corresponding cyclopropyl ketone in 40% yield[135]:



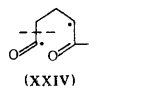
(XXII)

The lactone (XXIII) containing an exocyclic double bond isomerised into a bridged diketone (cf. isomerisation of unsaturated δ-lactones into 1,3-diketones in the presence of sodium methoxide, subsection 4)[153]:



(XXIII)

The most probable mechanism of isomerisation is that the diradical (XXIV), resulting from the lactone (XXII), is then stabilised by the elimination of carbon monoxide with formation of a three-membered ring; the diradical (XXV), formed from the lactone (XXIII), is stabilised as the dicarbonyl compound:



(XXIV) (XXV)

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The above survey makes it clear that investigations during recent years have revealed the great reactivity of unsaturated δ-lactones. The two main types of reactions studied (with preservation and with cleavage of the lactone ring) exhibit the peculiarities of the chemical behaviour of these compounds, which are determined by the vinyl position of the double bond relative to the heteroatom.

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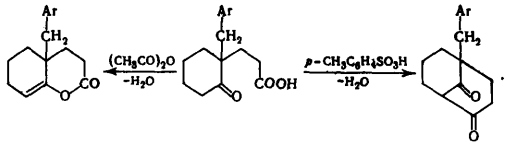
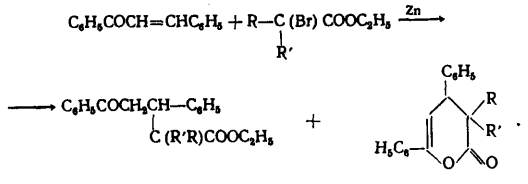
Papers have appeared since this review was submitted for publication which must be considered, if only very briefly, since they are directly concerned with the subject-matter of the present survey.

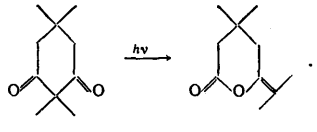
The lactonisation of δ-keto-acids has been described by the action of acetic anhydride[154,155], by the action of this reagent containing added toluene-*p*-sulphonic acid, and also by heating with toluene-*p*-sulphonic acid in tetralin solution[156]. The last method of dehydration, which was applied to β-(1-benzyl-2-oxocyclohexyl)propionic acids, led unexpectedly to the formation of bridged diketones, whereas the action of acetic anhydride on these keto-acids yields the normal dehydration products—unsaturated δ-lactones[157]:



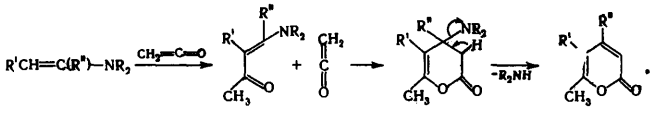
Unsaturated δ-lactones have been obtained from the Reformatsky reagent and αβ-unsaturated ketones, by spontaneous cyclisation of the δ-keto-esters formed directly[158]:



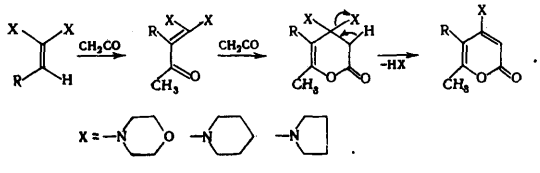
The photochemical conversion has been described of a substituted cyclohexane-1,3-dione into a δ-lactone containing an exocyclic double bond (the reverse reaction to the isomerisation of unsaturated δ-lactones into 1,3-diketones described in Section III, subsections 4 and 8)[159]:



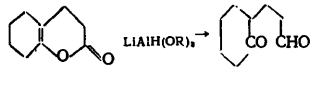
Unsaturated δ-lactones can be obtained by the interaction of acylated enamines with keten, and are easily further converted into 2-pyrones[160]:



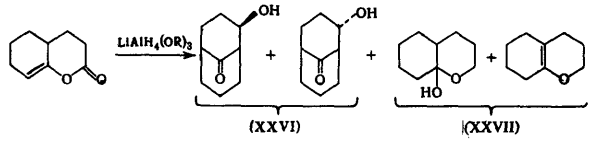
Keten reacts similarly with 1,1-diaminoethylenes to form unsaturated 4,4-diamino-lactones[161]:



Martin et al.[116] have shown that 3,4-dihydro-5,6-cyclohexano-2-pyrone is reduced by lithium hydrotri-t-butoxyaluminate to a δ-keto-aldehyde (without rearrangement of the carbon skeleton—cf. Section III, 2):



whereas the isomeric lactone containing an exocyclic (relative to the lactone ring) double bond will give under these conditions a mixture of reduction products obtained with (XXVI) and without (XXVII) rearrangement of the carbon skeleton (cf. Section III, 2):



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Fast Complexing Reactions

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CONTENTS

I. Introduction 209
II. Experimental methods of studying fast complexing reactions 209
1. Flow methods 210
2. Relaxation methods 212
A. Methods involving step perturbation 213
B. Methods involving periodic perturbation 214
C. Electrochemical methods 215
D. Other methods 215
III. Fast complexing reactions 216
1. Rate of nucleophilic substitution reactions 216
2. Rate of dissociation of complexes 219
3. Influence of stereochemical factors 219
IV. Reactions having an S_N mechanism 219
1. Reactions involving elements of Group I 219
2. Reactions involving elements of Group II 220
3. Reactions involving elements of Groups III-VI and manganese 220
4. Reactions involving elements of the iron group 221
V. Reactions having an S_E mechanism 221

I. INTRODUCTION

A division of metal complexes into "inert" and "labile" appeared very early in the development of the chemistry of complex compounds. The "inert" complexes included compounds of tervalent cobalt and chromium, the platinum metals, and certain others. These compounds are characterised by the slowness of their formation and breakdown; it was on these that the various types of isomerism and the important reactions of complexes were studied. Research on the kinetics and the mechanism of changes undergone by these compounds has been especially widely developed during recent years[1].

However, the so called "labile" complexes remained outside the scope of contemporary kinetic methods, and all reactions involving them were described as "instantaneous". There are considerably more "labile" than "inert" complexes, and the kinetics of complex formation thus covered a relatively small proportion of known reactions.

During recent years kinetic methods of investigation have appeared which enable reactions to be studied having a half-life period $t_{1/2}$† of 10^{-9} to 10 s,[2,3] i.e. over a considerably wider range (10^{10}) than for reactions occurring at the customary rates (10–10^4 s). With the appearance of these methods the reactions of the "labile" complexes became accessible to investigation. The first results obtained already show the promise of this branch of chemical kinetics.

Quite a large amount of experimental information has now accumulated on the kinetics of fast reactions. Two symposia have been devoted to these matters, the proceedings of which have been published in special issues of journals[4,5].

† The half-life period is the time during which half the initial concentration of a substance, a deficiency of which has been taken, is used up.

Methods of investigating fast reactions in solution and some of the available experimental information have been discussed in two large monographs[6,7]. There are good reviews of individual aspects of the kinetics of fast reactions[8-10] and reactions involving complex formation[11-15]. However, a sufficiently complete critical review of methods and experimental results on the kinetics of fast complexing reactions in solution is lacking. The present paper is intended to fill this gap.

II. EXPERIMENTAL METHODS OF STUDYING FAST COMPLEXING REACTIONS

All existing methods of investigating fast complexing reactions can be divided into a few large groups—flow methods, relaxation methods with step perturbation, relaxation methods with continuous perturbation, nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) methods, and electrochemical methods—which are compared in Table 1.

Table 1. Characteristics of methods for studying fast complex-forming reactions.

Methods	Limits of applicability, (time, s)		Soln.vol. for a kinetic curve
	min.	max.	
Classical methods	10	10^5	0.1—10 ml
Flow methods	10^{-4}	10	0.1 ml — 2 litres
Relaxation methods			
(*a*) step methods	10^{-7}	1	0.1—10 ml
(*b*) ultrasonic absorption	10^{-7}	10^{-4}	0.2—100 litres
Nuclear magnetic resonance	10^{-9}	10^{-1}	0.1—1 ml
Electrochemical methods	10^{-6}	1.0	1 ml

Flow methods, which are widely employed in studying reactions having half-life periods from 0.001 to 10 s, are the simplest from the point of view of apparatus, and are the only methods which enable kinetic curves for the processes to be obtained directly.

1. Flow Methods

The characteristic feature of flow methods is that solutions of the reactants are fed continuously to a special mixer, after which the reaction solution, in the form of a homogeneous, constant-velocity stream, enters an observation tube.

The course of the reaction can be followed firstly by using some physicochemical method to measure the reactant concentrations along the observation tube, in which the flow speed of the reactants is constant throughout the time of the measurements. In this case the distance from the mixer to the point at which the variation in reactant concentrations is recorded is proportional to the time which has elapsed from the start of the reaction to the instant of observation. Secondly, by halting the flow abruptly, we can use a suitable transducer and a rapid-acting device to record the variation in reactant concentrations, after the flow has been stopped, at any point in the observation tube. These two methods of measurement are termed the "constant-flow method" and the "stopped-flow method" respectively.

There are also a few methods which possess elements of both constant-flow and stopped-flow methods. Among these we have arbitrarily included accelerated-flow and quenching methods in the first group, and the method of removable partitions in the second.

The most crucial unit in the flow apparatus is the mixer. The design of the mixer determines the time of mixing of the reactant solutions, which determines the lower time limit of the flow apparatus [16,17], since the time of mixing must be much shorter than the half-life period of the reaction.

Among known designs, relatively simple mixers are most often used, with the solutions fed tangentially, these being employed for the study of reactions in which $t_{1/2} \geqslant 10^{-3}$ s. This is probably the limiting time for such mixers [16,18], since they have a special mixing chamber, preceding the observation tube. The presence of this chamber makes it impossible to define the instant of complete mixing. For the study of more rapid reactions, promise is shown by mixers having more than one channel for introduction of the reactant solutions, the minimum time of mixing being 10^{-4} s. [19]

Kletinik [18], by using a special bellows-type mixer, was able to shorten this time to 5×10^{-5} s. The disadvantage of this mixer is that it is made of metal foil, which may affect the kinetics of the reaction under investigation.

The functioning of the mixer can be tested in several ways [7]. The "chemical" method consists in determining the completeness and time of mixing of the reactant solutions in the mixer by means of a very fast chemical reaction, e.g.

$$H^+ + OH^- \rightleftarrows H_2O, \quad (1)$$

$$I_2 + 2S_2O_3^{2-} \rightleftarrows S_4O_6^{2-} + 2I^-. \quad (2)$$

In the "physical" method liquids differing in refractive index are mixed. In both cases the flow of solution should be homogeneous throughout the length of the observation tube following the mixer. A test method which uses a standard reaction is widely used, and is the most reliable of existing methods. The reaction chosen as standard is very often [6,7]

$$H_2CO_3 \rightleftarrows CO_2 + H_2O. \quad (3)$$

(*a*) Constant-flow methods. With constant-flow apparatus the solution, after leaving the mixer, enters the observation tube at a constant rate. The time t_n (in seconds) required for the liquid to reach a plane n crossing the observation tube is then given by the equation [18]

$$t_n = \frac{l_n}{R} \quad (4)$$

where R (mm s^{-1}) is the flow speed, while l_n (mm) is the distance from the plane of mixing to the point of observation, and the time elapsed after mixing is proportional to the length of the observation tube. With a known flow speed R, it is possible to determine the time from the start of the reaction to the instant of observation at the points n. By measuring the reactant concentration at these points by some physical method, we can obtain the kinetic curve for the given reaction.

The minimum time of reaction which can still be recorded on a constant-flow apparatus will depend on the design of the mixer and the rate of flow in the observation tube, but increasing the flow speed above 10 m s^{-1} may result in cavitation [20].

The solutions can be supplied to the mixer either by gravity feed [21], by means of compressed gas [22-24], or by means of syringes [25].

Among physical methods for recording the variation in concentration in the observation tube, spectrophotometric methods are most often employed [26-30].

In the simplest types of apparatus, light filters are used as monochromators, while the sensors are photocells connected to a measuring instrument, usually a galvanometer [26-30]. Such instruments are usually of low sensitivity and small resolution. The variation in light absorption along the observation tube is recorded from the galvanometer readings, which results in diminished accuracy, increased time of measurement, and hence considerable consumption of the reactant solutions. With the use of monochromators of greater dispersion, flow apparatus having spectrophotometric recording is employed for the study of complicated chemical reactions. Thus with a Beckman spectrophotometer as monochromator it was possible to establish that at least six different processes occurred in the oxidation of sulphurous acid by iodine [32,33].

A double-beam apparatus has been described [34]. The most perfect instrument of this type has been described in Ref. 25. Its distinguishing feature is that the absorption spectra of the test solution at definite points in the observation tube are recorded by means of a monochromator and a photomultiplier, the latter connected to an electronic oscillograph, the screen of which can be photographed with a high-speed cine-camera. If spectrophotometric methods are to be applied, of course, the light absorption of the test solutions must change in the course of the reaction. This somewhat restricts the use of such apparatus.

Great versatility is shown by apparatus having thermometric transducers, which are moved inside the observation tube by means of a special device or—what is not as good—are fixed in the tube, when a certain relation must exist between the size of the transducer and the internal diameter of the tube [17]. The sensitivity of instruments in which the thermocouple current is not amplified is very

low, so that only reactions whose heat of reaction exceeds 20 kcal mole^{-1} can be studied with such apparatus. Their sensitivity can be considerably improved by using thermistors [35-39] or d.c. photoelectric amplifiers [40] as transducers. An apparatus of this type described by Perlmutter-Hayman [41] has enhanced sensitivity, is convenient in operation, and requires a relatively small quantity of reactant solutions.

Reactant concentrations in the observation tube can be determined also from conductivity measurements [18,22-24,42], potentiometrically [43-45], and by the n.m.r. method [46,47]. This last method is very promising for the study of complicated chemical reactions, since it permits the unambiguous identification of many intermediate products and changes occurring in the reactant molecules or ions.

The accelerated-flow and quenching methods can be included in the constant-flow method. In the former [48,49] the transducers are fixed at a certain point in the observation tube, whereas the flow speed changes during observation. Both the variation in the flow speed and that of the reactant concentrations with time are recorded oscillographically. The results can be used to plot a kinetic curve for the process. Considerably less solution is required to determine the kinetic curve in the accelerated-flow method than in the other constant-flow methods.

In the quenching method [50-55] the solution of the reactants, after leaving the mixer and flowing through the observation tube, is rapidly mixed with a "stop solution". Ordinary analytical methods are used to determine, in the reaction mixture "frozen" in this way, the change occurring in the reactant concentrations during the time required for the reactant solution to pass from the first to the second mixer, where this solution is mixed with the "stop solution". This time is governed by the dimensions of the tube and by the flow speed.

The apparatus for the quenching method is very simple, while the reactant concentrations can be determined by ordinary analytical methods (gravimetrically or by titration) with great accuracy. The quenching method is widely used for the study of intermediate products, and also in investigating various exchange reactions.

(*b*) Stopped-flow methods. Whereas about a litre of reactant solution is required to plot the kinetic curve when constant-flow apparatus is used, stopped-flow apparatus requires only a few tenths of a millilitre of the reactant solutions for this purpose, and the whole kinetic curve can be obtained from a single experiment. This considerably facilitates working with expensive, rare reagents, but more complicated apparatus is employed in the stopped-flow method.

In such apparatus [56] the rapid flow of reactant solutions is abruptly halted at a certain instant. At the same instant a recording device, connected to a transducer fixed in the observation tube near the mixer, registers the time variation of the reactant concentrations in the halted stream. The reactant solutions are fed to the mixer and the observation tube from syringes, whose pistons are interconnected and are moved by hand, a spring, or an electric motor.

The stream is halted either by abruptly stopping the syringe pistons or by means of special valves following the observation tube [57,58]. The last method is the most reliable, since it excludes entry of solution into the observation tube after the flow has been stopped, e.g. because of possibly play in the mechanical system feeding the solutions.

In all the forms of apparatus described in the literature the kinetic curve is recorded on an oscillograph, triggered either by means of a special photoelectric device [57] or by electromechanical means. The variation in concentration of the reactant solutions is recorded photoelectrically [57-61]. The most perfect apparatus operating by the stopped-flow method with spectrophotometric recording has been described by DeSa and Gibson [62]. Using a double-beam spectrophotometric arrangement with modulated light flux, these workers considerably improved the sensitivity (to 10^{-3} unit of optical density) and lowered the noise level.

The electrical-conductivity [60] and potentiometric [40-42] methods are seldom used in stopped-flow apparatus. Thermometric transducers are not employed here because of their great inertia. However, fine-wire thermocouples [63], having considerably less inertia, can be used in this type of apparatus.

Among these methods can be included the removable partition method, proposed by Connick and his coworkers [64,65] for studying the kinetics of reactions occurring in very dilute solutions, since in this case long cuvettes can be used for observation. As in the stopped-flow method, the solutions are rapidly mixed and the reaction is followed oscillographically, but the removable-partition method differs greatly in the mode of mixing and the construction of the cuvette for observation by the stopped-flow method.

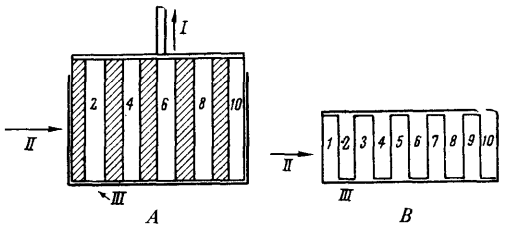

Figure 1. Diagram of cuvette for removable-partition method: *A*) side-view; *B*) plan; *I*) direction of movement of partition by action of spring; *II*) direction of observation; *III*) body of cuvette; *1, 2, 3, 4, ...*) compartments of cuvette.

The cuvette illustrated in Fig. 1 has a movable partition dividing the whole cuvette into a series of compartments (ten in the illustration), with one reactant solution in the even compartments, and the other in the odd compartments. This partition can be removed (upwards in the diagram) by means of a spring, and then the solutions in the isolated compartments will rapidly mix (within 10^{-3} s) and the variation in light absorption of the test solution will be recorded on an oscillograph.

Table 2 gives brief technical characteristics of the types of apparatus designed for the study of fast chemical reactions by flow methods. It is seen that these methods are suitable for reactions having half-reaction times of 10^{-4} to 1 s.

There is little prospect of constructing new mixers and increasing the flow speed to shorten the lower time limit for flow apparatus.

The use of non-aqueous solvents and lowering the temperature of the reactant solutions [66,67] permits the study of reactions which are very fast at 25°C (having rate constants of $\sim 10^6$ M s^{-1}) by existing flow techniques.

A very interesting possibility is the use of magnetic recording instead of photographing oscillograms, which is used to obtain kinetic curves in existing apparatus operating by the stopped-flow method [68].

In the study (by the stopped-flow method) of complicated reactions involving coloured substances, great opportunities are offered by high-speed spectrophotometric instruments, which enable the spectra of substances taking part in processes occurring within 10^{-6} s to be photographed[69].

Table 2. Characteristics of flow methods.

Methods	Limiting time × 10^3, s	Soln. for a kinetic curve, ml	Temp. range, °C	Absorbing layer, mm	Material of mixer	Measurement of concn.
Constant-flow methods	0.1-1		0-50	1-5	glass, plastic, brass	spectrophotometric, conductivity, heat effect
(*a*) Visual readings		500-2000				
(*b*) Automatic recording		6-100				
Accelerated flow	1.0	0.1	10-30	2	plastic	colorimetric
Quenching	10	100	10-50		plastic, glass	any analytical method
Stopped flow	2-5	0.1-1.0	-120 + 40	1-10	glass, plastic	colorimetric, spectrophotometric, potentiometric, conductivity
Removable partitions	15	30	14-30	50	steel	colorimetric

Flow methods (especially the stopped-flow method) are widely used to study the kinetics of fast complexing reactions. Reactions involving the ions of copper[70], iron[71,72], and nickel[73] have been studied in especial detail by these methods.

Among methods for measuring concentrations, the spectrophotometric method has become the most widely used, being the simplest but sufficiently widely applicable and sensitive.

Complex formation is mostly studied in the presence of a large excess of foreign electrolytes, which makes it difficult to use conductivity measurements to determine the reactant concentrations, since existing instruments permit the kinetic curve of a reaction to be recorded only if the change in conductivity occurring during the reaction exceeds 10%. With the use of special amplifiers[74], however, this limit has been lowered to 0.1%, which has enabled the complexing reaction

$$Be^{2+} + HF \rightleftarrows BeF^{+} + H^{+} \qquad (5)$$

to be studied in 0.2 M potassium chloride solution. This opens up wide prospects for the study of various complexing reactions, especially those which are not accompanied by a change in light absorption.

Concluding this survey of flow methods, we must note that these methods can be applied to the study of chemical reactions having $t_{1/2} > 10^{-4}$ s.

Apparatus having a constant flow and electrometric transducers is most simply constructed. For the study of multistage reactions involving coloured substances, more complicated spectrophotometric recording is most often employed, enabling the kinetics of conversion of any of the coloured substances involved in the reaction to be studied directly.

If, however, it is necessary to work with a small consumption of reactants, more complicated apparatus is used, operating by the stopped-flow method, which has the same characteristics as constant-flow instruments, but requires less than 1 ml of reactant solutions for the determination of one kinetic curve.

2. Relaxation Methods

At the present time only relaxation methods permit direct observation of the course of chemical reactions occurring in times less than 10^{-4} s, which considerably facilitates the study of multistage processes of complex formation, such as, for example[75],

$$Co^{2+} + gly \rightleftarrows [Co(gly)]^{+}, \qquad (6)$$

$$[Co(gly)]^{+} + gly^{-} \rightleftarrows [Co(gly)_2], \qquad (7)$$

$$[Co(gly)_2] + gly^{-} \rightleftarrows [Co(gly)_3]^{-}. \qquad (8)$$

(gly = the glycine ion)

A serious limitation of these methods is that they are applicable only to equilibrium processes when the equilibrium has not been displaced too far in the direction of formation of the reaction products.

In relaxation methods a system in a state of dynamic equilibrium is by some means brought out of this equilibrium. After cessation of the disturbing action, a process tending to re-establish the original equilibrium begins in the system. This process is termed relaxation. Relaxation curves are described by the equation

$$I = I_0 e^{-\frac{t}{\tau}}, \qquad (9)$$

where I_0 and I are parameters, which vary linearly with the concentration of an indicator substance, at times t_0 and t respectively, and τ is the relaxation time, which defines the rate of relaxation and is given numerically by the time required for I_0 to change by a factor e. The chemical equilibrium can be disturbed by varying certain physical parameters, such as temperature, pressure, electric field strength, etc.

The relaxation resulting from chemical processes is usually recorded from the variation in the light absorption or the electrical conductivity of the test solution.

With the relaxation time τ known, we can use the mathematical procedure suggested by Eigen[76-79] to calculate the rate constant of the processes under investigation. Thus for a reaction of the type

$$AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B \qquad (10)$$

for example, the relaxation time is given by the equation

$$\tau^{-1} = (k_1 + 2k_{-1} X_e) \qquad (11)$$

where k_1 and k_{-1} are the rate constants of forward and reverse reactions respectively, and X_e is the equilibrium concentration of the species A and B, provided that [A] = [B].

If the equilibrium constant of (10) is unknown, k_1 and k_{-1} can be determined from the dependence of τ on the concentration of the species AB. When the equilibrium constant

is known, the rate constant k_1 is calculated for the same cases by means of the equation‡

$$k_1 = [\tau([A] + [B] + K]^{-1} . \quad (12)$$

Here [A] and [B] are the equilibrium concentrations of the species A and B, and K is the equilibrium constant corresponding to Eqn. (10). Equation (12) is valid provided that the concentrations [A] and [B] differ at most by a factor of 100. The rate constant k_{-1} for formation of AB is calculated from the equation

$$k_{-1} = \frac{k_1}{K} . \quad (13)$$

Relaxation methods can be divided into two groups—involving step and continuous perturbation—according to the mode of varying the physical parameters disturbing the chemical equilibrium. The first group includes methods involving abrupt changes in electric field strength, pressure, or temperature, as well as the abrupt change of concentration suggested recently[80].

A. Methods Involving Step Perturbation

(*a*) Temperature-jump method. This method is mostly widely used and widely applicable of the relaxation methods described in the literature. It can be employed for equilibrium reactions which are accompanied by a thermal change. The temperature variation of the equilibrium constant K is given by the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT} \quad (14)$$

where T is the temperature and ΔH the heat of reaction. Relaxation curves are recorded oscillographically from the variation in the light absorption or the electrical conductivity of the solutions.

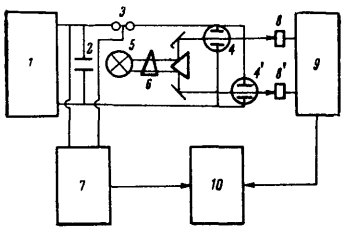

Figure 2. Diagram of apparatus for studying the kinetics of chemical reactions by the temperature-jump method.

For ionic solutions a jump in temperature is achieved by means of a pulse discharge from a capacitor charged to a high voltage[79,81-83]. Fig. 2 shows a simplified diagram of the forms of apparatus used, proposed by Eigen and his collaborators. A high-voltage current source *1* charges the condenser *2* of capacitance 0.1 μF to a voltage at which discharge takes place across the spark gap *3* and through cuvettes containing the test solution *4* and the reference solution *4'*. Platinum electrodes are inserted into the cuvette containing the test solution, of volume 50 ml, in such a way that ~ 1 ml of the test solution lies between them. During the high-voltage discharge, which lasts a few microseconds, the solution between the electrodes is heated by approximately 10 deg. The relaxation curves are recorded by means of a photocolorimetric device consisting of a light source *5*, a monochromator *6*, and photomultipliers *8* and *8'* connected differentially. The amplifier *9* is connected to an electronic oscillograph *10*, triggered by the release device *7*. The rate constant of the processes which occur can be calculated from the variation in optical density of the solution during relaxation[6,7].

It is very important that the duration of the pulses should approximate to the relaxation time. If the duration θ of a pulse differs markedly from the relaxation time of the process under investigation, the error involved in the measurements is considerably increased. The way in which the ratio τ/θ affects the character of the relaxation observed is shown in Fig. 3.

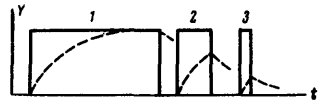

Figure 3. Variation in relaxation signal (broken curve) for periodic pulses (pulse signal represented by full line)—where Y is the magnitude of the signal and t is the time—as a function of the ratio of the duration of the pulse to the relaxation time (θ/τ):
1) 4; *2*) 1; *3*) 0.25.

In apparatus intended for the kinetic study of fast chemical reactions using a temperature jump produced by the discharge of a capacitor (as e.g. in the above apparatus of Eigen's), it is very difficult to vary the duration of the pulse or control its amplitude. An apparatus[84] in which the solution is heated by a powerful high-frequency pulse taken from a magnetron oscillator is free from this defect. This apparatus can be used also to study reactions occurring in non-ionic solutions, where the Eigen method is inapplicable. A periodic temperature-jump apparatus was constructed using repeated high-frequency pulses to heat the test solution[85], which both increased the output of the investigator and improved the reliability of the results, but unfortunately the size of the jump obtainable was small (~ 1 deg).

Equipment combining the flow method with the temperature-jump method is very promising for the study of complicated multistage reactions and also fast irreversible processes[86,87].

(*b*) Electric field-pulse methods. The electrical conductivity of a weak electrolyte increases with increase in the electric field strength. This phenomenon has been termed the Second Wien effect[88]. It is explained by a shift in the equilibrium—weak electrolyte molecule-ion-pairs-free ions—towards formation of free ions.

‡ It would seem that this equation should read

$$k_1 = K\tau^{-1}([A] + [B] + K)^{-1}$$

(Ed. of Translation).

The increase in conductivity is proportional to the applied voltage between 40 and 100 kV cm^{-1}. The total increase may reach 10% of the conductivity in the absence of an electric field. The magnitude of the change is given by the equation[89]

$$\frac{\Delta\lambda}{\lambda_0} \equiv \frac{\lambda_x - \lambda_0}{\lambda_0} = \frac{1-\alpha}{2-\alpha} \cdot b\Delta E \qquad (15)$$

where λ_x and λ_0 are the conductivities of the solution in a field of strength x and in zero field, $\alpha = c_i/c_0$ is the degree of dissociation under the influence of the field, c_i being the concentration of ions formed under the action of the field and c_0 the total concentration of the weak electrolyte, E is the strength of the field, and b is a parameter depending on the mobility of the ions, the absolute dielectric constant, and the temperature.

The electric field–pulse method was first used by Eigen and his coworkers in studying the kinetics of the reaction[76,90-92]

$$H^+ + OH^- \rightleftarrows H_2O. \qquad (16)$$

Relaxation curves are mostly recorded from the variation in conductivity, and the experimental results obtained are processed by the usual methods described previously.

(*c*) Pressure-shock methods. The effect of pressure on the equilibrium constant is represented by the equation[9]

$$\beta = \exp\left[\int_{P_1}^{P_2} (\partial \ln K/\partial P)_s dP\right] = \exp\left[\int_{P_1}^{P_2} \frac{-\Delta V^0 + \Delta H^0 (\partial V/\partial T)_p C_p}{RT} dP\right] \qquad (17)$$

where ΔV^0 and ΔH^0 are the changes in volume and enthalpy, and $\beta = K_2/K_1$, in which K_2 and K_1 are respectively the equilibrium constant at $P = P_2$ and $P = P_1$: a change in pressure thus produces a change in the equilibrium constant, as a consequence of which relaxation processes occur at a rate determined by that of the chemical reactions involved[93-95].

The magnitude of the shift β is 0.004 with $\Delta V^0 = 1$ cm^3 $mole^{-1}$ and a change in pressure from 1 to 100 atm[96]. This shift can be easily recorded by various physicochemical methods.

The types of apparatus used in this method differ both in the way in which the pressure is changed and in the method adopted to measure the reactant concentrations during the relaxation process.

The pressure can be changed by opening a special tap connecting an autoclave to a cylinder containing compressed gas[96]. Since this tap is opened manually, reactions having a half-period exceeding 0.1 s can be studied with such apparatus.

A more modern method of producing a pressure shock[97] consists in rapidly puncturing with a special steel needle a thin steel diaphragm fitted in the system connecting the compressed-gas cylinder with the autoclave containing the test solution. As a result, the pressure in the autoclave drops sharply (within 10^{-5} s). As the workers who have used this method state, reactions can be studied having $t_{1/2} > 10^{-5}$ s.

In all the types of apparatus described, the reactant concentrations are determined either from conductivity measurements or spectrophotometrically.

The great advantage of the pressure shock method is the possibility of studying directly conversions of outer-sphere into inner-sphere complexes and conversely, which is impossible by any other method with the exception of n.m.r.

B. Methods Involving Periodic Perturbation

Fast chemical reactions can be studied not only by pulse methods but also by methods involving a periodic action. Among these, ultrasonic absorption and nuclear magnetic resonance have become the most widely used.

(*a*) Ultrasonic absorption. By means of ultrasonic vibrations it is possible to study chemical reactions whose duration approximates to the period of the sound wave. The frequency dependence of the absorption of sound is influenced by the changes in free energy, entropy, and volume occurring during the reaction, and also by the rates of the chemical reactions taking place in the system[98-101], so that both kinetic and thermodynamic data can be obtained by studying the ultrasonic absorption of the test solution[89,102].

For single-stage reactions the ultrasonic absorption–frequency curve passes through a maximum, the position of which can be used to determine the relaxation time, and from which the reaction rate constant can be calculated by means of Eqns. (11) and (12). With multistage reactions the mathematical processing of the experimental results is considerably more complicated[103,104]. There exists a method of calculation which is applicable only to a two-step process[105,106].

The equipment used in the study of fast chemical reactions by the acoustic method is that usually employed for measuring the velocity and absorption of ultrasound in liquids[60,107,108]. The disadvantages of this method include the relative complexity of the apparatus used, the difficulties of processing the experimental results for complicated reactions, and also the large quantities of solutions necessary for an experiment.

(*b*) Nuclear magnetic resonance. The n.m.r. method is applicable to the kinetic study of chemical reactions occurring at very varied rates. The essence of the method is that, if an atomic nucleus possessing a magnetic moment is placed in a homogeneous magnetic field, its energy levels will be split, and energy quanta may be absorbed or emitted on transition of the nucleus from one split level to another. The magnitude of this splitting will depend on the degree of nuclear screening, which is determined by the nature of the chemical compound formed. Reactions occurring at normal rates can be studied from the time variation in the intensity of the absorption band, while the change in shape of the absorption bands, in particular their broadening, will provide information on the kinetics of reactions which are 50% complete in 10^{-8} s.

Details of the apparatus employed in n.m.r. investigations of fast reactions and of methods of calculating rate constants from experimental results can be found in numerous monographs and reviews on this topic[6,7,104,109-114].

The n.m.r. method has found especially wide use in the study of fast exchange reactions. This requires that the parameters of these n.m.r. absorption bands should be known for the compounds in the absence of exchange. Such data can be obtained, for example, by determining the n.m.r. spectra of the pure compounds. In the case of rapid exchange, the absorption bands of the individual compounds become wider, and at a certain rate they merge into a single broad band, which gradually narrows with increase in the rate of exchange.

The coalescence of absorption bands with rapid exchange can be explained by means of the uncertainty principle,

which in the present case can be written in the form

$$\tau \Delta\nu \approx {}^1/_2\pi , \qquad (18)$$

where $\Delta\nu$ is the distance (in cm^{-1}) between the resonance signals and τ is the shortest time in which these signals still exist separately.

From the shape of the band observed and also its broadening compared with the bands of individual compounds, the rate of exchange can be found [104].

To obtain more accurate data, and also to determine the order of the reactions, the exchange velocity is increased, by altering certain parameters (temperature, catalyst concentration), until the absorption band maxima corresponding to the different chemical shifts coalesce. The rate constant of the reaction is determined from the position and shape of the resulting band, and the order of the reaction is found from the dependence of the broadening $\Delta\nu$ of the band on the variable parameter P. Four cases can be distinguished [115,116] according to the nature of the dependence (Fig. 4).

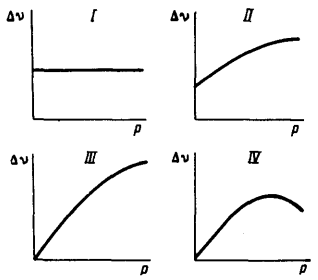

Figure 4. Dependence of $\Delta\nu$ on a parameter P for various types of chemical reactions.

With the type of dependence of $\Delta\nu$ on the parameter P represented by case I (Fig. 4), exchange is very slow. Only "outer-sphere relaxation" occurs, when species in the outer sphere take part in the relaxation process [117]. This type of relationship is observed, for example, with the ethylenediamine complexes of nickel.

In case II the curve obtained does not start from zero, as is possible when first-order and second-order reactions are occurring simultaneously in the system. This relationship can be used to calculate the rate constants of both reactions, as has been done [115] for the glycine complexes of tervalent cobalt and iron.

Case III corresponds to second-order reactions, whereas case IV is observed when variation in the parameter P is accompanied by variation in the concentration of species which make different contributions to the broadening of the absorption band. Case IV is observed with many compounds of bivalent copper [115].

The possibilities of the n.m.r. method in the study of complicated reactions can be considerably extended by using it with flow apparatus [46].

It must be noted that the n.m.r. method is applicable (when the change in shape of absorption bands is used to determine the rate constant) only for the study of very fast reactions of complex formation (having $t_{1/2} < 10^{-4}$ s) in equilibrium systems involving elements whose nuclei have spins differing from zero.

C. Electrochemical Methods

A group of phenomena are known in polarography in which the main electrochemical process of reduction of the depolariser is preceded by chemical reactions occurring in the layer adjacent to the electrode, as a result of which either depolariser is regenerated or it is formed from compounds which are not reduced under the given conditions. As a result of these processes polarographic currents arise which are different in nature from diffusion currents [118], and are termed catalytic or kinetic currents. The magnitude of both catalytic and kinetic currents will depend on many factors, in particular the rate of the chemical reactions associated with the electrochemical process [119,120].

For coupled processes of the type

$$M^{n+} + L \rightleftarrows ML^{n+} , \qquad (19)$$

$$ML^{n+} + me = ML^{(n-m)+} \text{ (on the electrode)} . \qquad (20)$$

Brdička and Wiesner [119] deduced the approximate equation

$$\mu k_1 = \frac{i_{cat}}{nFq10^3 C_M (aC_L - i_{cat})} \qquad (21)$$

linking the strength of the catalytic current with the rate constant k_1 of reaction (19), in which n is the number of electrons involved in the electrochemical process, F is Faraday's constant, q is the mean surface area of the mercury drop, i_{cat} is the maximum catalytic current (in μA), $a = 605nD_L^{1/2}m^{2/3}t^{1/6} \times 10^3$ is the Ilkovič constant, and μ is the thickness of the layer adjacent to the electrode, in which chemical reaction occurs.

For analogous chemical reactions Koutecký [120] linked the rate constant of the chemical reaction with the catalytic (kinetic) current by the more accurate equation

$$\frac{i_{kin}}{i_{diff}} = \frac{0.886\,[(k_1/K)\,t]^{1/2}M}{1+0.886\,[(k_1/K)\,t]^{1/2}M} - \frac{11D^{1/2}m^{-1/2}t^{1/2}(k_1t/K)^{1/4}M^{1/2}}{1+0.14\,(k_1t/K)\,M^2} , \qquad (22)$$

where i_{kin} is the kinetic current, i_{diff} is the diffusion current, $K = k_2/k_1$ is the equilibrium constant of (19), with k_1 the rate constant for formation of the complex ML^{n+} and k_2 the rate constant for dissociation of this complex, m (in mg s^{-1}) is the mercury drop rate, t (s) is the lifetime of a drop,

$$D = (D_M + KD_L)(1 + K) \text{ and } M = (D/D_L)(D_M/D_L)^{1/2}$$

in which D_M and D_L are the diffusion coefficients of the metal ion and the ligand respectively. Equation (22) holds provided that $K \gg 1$ and $(k_1 + k_2)t \gg 1$, i.e. for relatively fast reactions. Tabulated values of the function (22), found by Koutecký and Čižek [121], can be used to calculate the rate constant of reaction (19) from experimental data.

Rate constants of simple chemical reactions of the first and second order can be calculated in a similar manner. If, however, the reaction taking place in the reaction layer is complicated or of order higher than the second, it is difficult to use electrochemical methods to determine the rate constants of fast reactions. Furthermore, the results obtained have poor reproducibility, and require a large excess of the ligand and of foreign substances.

D. Other Methods

Besides the above methods, fast chemical reactions in solution are studied also by concentration relaxation [80],

flash photolysis[122] and radiolysis[123], and pulse conductivity[94]. The rate constants of ultrarapid reactions (having half-conversion periods of 10^{-14}–10^{-11} s) can be calculated from the line broadening in the Raman spectra[124,125]. These methods have not yet become widely used for the study of fast complexing reactions.

III. FAST COMPLEXING REACTIONS

Most cases of complex formation can be regarded as multistage processes, in which the chief part is played by substitution reactions. In aqueous solution all ions are hydrated, so that even with simple electrostatic interaction it is most probable that the formation of complex species involves several stages, for example

$$M^+aq + L^-aq \rightleftarrows [M^+aq][L^-aq] \quad (23)$$

(formation of ionic association complexes),

$$[M^+aq][L^-aq] \rightleftarrows [M^+aqL^-] \quad (24)$$

(formation of ion-pairs),

$$[M^+aqL^-] \rightleftarrows [ML] + aq. \quad (25)$$

It has been shown by various methods that the formation of association (outer-sphere) complexes is controlled by diffusion processes, and has a rate constant of the order of 10^8–10^{10} s^{-1}. In many cases the rate-determining stage is the conversion of outer-sphere complexes into complex compounds containing ligands in the inner sphere (reaction 25); it is more affected than any other stage by the individual characteristics of the interacting species[12].

Substitution reactions involved in the formation of complex compounds can be of two kinds—replacement of one ligand by another or else of one metal ion by another in the complex compound—and in Ingold's proposed classification these types are termed respectively nucleophilic (S_N) and electrophilic (S_E) substitutions. The type of substitution is determined by the starting materials and the final reaction products. Most fast reactions of complex formation which have at present been studied are nucleophilic substitutions (S_N).

1. Rate of Nucleophilic Substitution Reactions

(*a*) Effect of nature of metal ion. The rate of a nucleophilic substitution is influenced by many factors, among the most important of which are the nature of the interacting ligand and the parameters of the central ion—electron configuration, size, and charge.

There is as yet no single reliable method of calculating the rate constants of fast reactions in solution. Existing theories explain only the relative change in rate constant with variation in some parameter. Among such theories those using an electrostatic approach and also the ligand field theory have become most widely known.

The electrostatic approach was first used by Debye[20,126], who applied Stokes' law to ionic reactions of the type

$$H^+ + OH^- \rightleftarrows H_2O$$

and found a relationship between the maximum possible rate constant and the electrostatic characteristics of the reactant species

$$k_{rt} = \frac{4\pi n Z_1 Z_2 e_0^2 (D_1 + D_2)}{10^3 \epsilon k T \left[\exp\left(\frac{Z_1 Z_2 e_0^2}{\epsilon k T \sigma}\right)\right]},$$

where $n = 6.022 \times 10^{23}$ $mole^{-1}$ is Avogadro's number, Z_1 and Z_2 are the charges on the ions (positive and negative integers), $e_0 = 4.80 \times 10^{10}$ $cm^{3/2}$ s^{-1} is the charge of the electron, D_1 and D_2 (in cm^2 s^{-1}) are the diffusion coefficients of the corresponding ions, ϵ is the dielectric constant, $k = 1.38 \times 10^{-16}$ erg deg^{-1} is Boltzmann's constant, T is the temperature on the Kelvin scale, and $\sigma = 7.5 \times 10^{-8}$ cm is the thickness of the reaction layer. This equation holds only for dilute solutions and reactions whose rate is controlled by the diffusion of the reactant ions.

With values of $D_i = 10^{-4}$–10^{-3} cm^2 s^{-1} and $\sigma = 1$–12 Å (i.e. values of these parameters characteristic of ordinary ions) the rate constant of complex formation calculated by means of Eqn. (26) may vary from 10^7 to 10^{10} $mole^{-1}$ s^{-1}. Such rate constants are observed with reactions involving ions of the alkali and alkaline-earth metals as well as certain ions of bivalent metals (Cd^{2+}, Hg^{2+}, Cu^{2+}) (see Tables 7–11, below).

The electrostatic theory can only in certain cases predict the variation in rate constant for a reaction involving ions having a complete electron shell, but it is unable to predict the variation in the rate constant in reactions involving ions of the transition metals. Thus, for example, it cannot explain the great difference in reaction velocities between the ions Fe^{3+} and Cr^{3+}, which have practically the same electrostatic characteristics.

Use of the crystal field and ligand field theory[127–131] for reactions involving transition-metal ions makes it possible in certain cases to calculate the energy characteristics of the initial and a possible transition state. Calculation of these characteristics helps us to foresee qualitative changes in activation energy, and therefore in the rate of complexing reactions involving transition elements.

The energy characteristics of a transition complex are determined mainly by its stereochemistry. To a first approximation the structure of the transition state can be determined from the mechanism of nucleophilic substitution, which may occur either by a unimolecular (S_N1) or by a bimolecular (S_N2) mechanism. In the former case a complex of coordination number 6 is converted into a complex of coordination number 5: i.e. an octahedral configuration passes into a square pyramid or a trigonal bipyramid. In the latter case a complex having the same coordination number is converted into a transition state of coordination number 7, which has the configuration of a pentagonal bipyramid. Which mechanism (S_N1) or (S_N2) is involved in a substitution can be determined from the pressure dependence of the rate constant[1] or from the electrostatic characteristics of the central field.

Table 3. Change in energy (in Dq units) when the initial complex compound passes into the intermediate complex for substitutions involving elements of the first transition period.

Electronic configuration	S_N1 mechanism octahedron → square pyramid		S_N2 mechanism octahedron → pentagonal pyramid		Electronic configuration	S_N1 mechanism octahedron → square pyramid		S_N2 mechanism octahedron → pentagonal pyramid	
	strong field	weak field	strong field	weak field		strong field	weak field	strong field	weak field
d^0	0.00	0.00	0.00	0.00	d^6	4.00	−0.57	8.52	−1.28
d^1	−0.57	−0.57	−1.28	−1.28	d^7	−1.14	1.14	5.34	−2.56
d^2	−1.14	−1.14	−2.56	−2.56	d^8	2.00	2.00	4.26	4.26
d^3	2.00	2.00	4.26	4.26	d^9	−3.14	−3.14	1.07	−1.07
d^4	1.43	3.14	2.98	1.07	d^{10}	0.00	0.00	0.00	0.00
d^5	0.86	−0.57	1.70	0.00					

Table 3, taken from the monograph by Basolo and Pearson[131], gives results of the approximate calculation of the change in energy accompanying the change in configuration

associated with the conversion of an initial complex compound into a transition state. The approximations of the crystal field method were used in the calculation. It is seen that the greatest change in energy is required for ions having d^3, d^6, and d^8 electronic configurations: i.e. reactions involving these ions have a greater activation energy, and should therefore be slower, than reactions involving other ions. This principle is supported by experimental data available in the literature (Table 4).

Table 4. Rate constants for complex formation by elements of the first transition period.

Electronic configuration	Ion	I* k, $M^{-1}\ s^{-1}$	II* k, $M^{-1}\ s^{-1}$	III* k, $M^{-1}\ s^{-1}$
d^0	Ca^{2+}	10^8	$7\cdot10^8$	$2\cdot10^7$
d^5	Mn^{2+}	$2\cdot10^7$	—	10^6
d^6	Fe^{2+}	$3\cdot10^6$	—	$6\cdot10^6$
d^7	Co^{2+}	$33\cdot10^5$	$4\cdot10^4$	10^5
d^8	Ni^{2+}	$3\cdot10^4$	$4\cdot10^3$	10^4
d^9	Cu^{2+}	$3\cdot10^5$	$1\cdot10^6$	10^5
d^{10}	Zn^{2+}	$2\cdot10^5$	$4\cdot10^6$	$3\cdot10^6$

* The reactions are represented by the equations

(I) $[M(H_2\mathring{O})_6] + H_2O \rightleftharpoons [M(H_2O)_6] + H_2\mathring{O}$

(II) $M^{2+} + day \rightleftharpoons [M(day)]^{2+}$

day = 2-*p*-dimethylaminophenylazopyridine

(III) $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$.

More detailed consideration of the dependence of reactivity on the electronic structure of the reactant ions from the viewpoint of crystal field theory suggests that the rate of complex formation should decrease in the sequence of ions having the electronic configurations—$d^5 > d^4 > d^3 > d^6$—for both S_N1 and S_N2 mechanisms. Unfortunately, many postulates were made in this calculation, and there are as yet no reliable experimental data supporting this hypothesis.

Qualitative results can be obtained by considering the influence of the Jahn–Teller effect on the reactivity of complex compounds [130-131]. This effect consists in the distortions arising in a symmetrical non-linear polyatomic molecule having a degenerate electronic state, as a consequence of which distortions the symmetry of the molecule is diminished [132]. Thus in the d^9 system (the Cu^{2+} ion), for example, there is one vacant e_g-orbital, whose axes pass through the central ion and opposite ligands. The absence of an electron in one of the e_g-orbitals diminishes the screening of the central ion, with a consequent increase in the strength of interaction between negatively charged ligands and the central ion, so that the distance between them becomes shorter. Either two or four ligands will move towards the central ion; correspondingly either two short and four long—or four short and two long—bonds appear in an octahedron, and the latter is converted into a bipyramid.

Ligands located farther from a central ion are more reactive, since the mobility of ligands increases with increase in the distortion. Hence the rate of substitution should be considerably smaller with highly symmetrical complexes than in less symmetrical complexes.

The dependence of the Jahn–Teller distortion, arising in an octahedral configuration, on the electronic structure of transition-metal ions of the first series is shown in Table 5. It is seen that the greatest distortion appears with the structures d^4 and d^9, so that complexes of Cr^{2+} and Cu^{2+} should possess the greatest reactivity. This principle is supported by available experimental data (Table 4).

Table 5. Distortion of octahedral complexes of transition metals of the first series (Jahn–Teller effect) [132].

Configuration	Symmetry	Expected distortion due to orbital degeneracy	Configuration	Symmetry	Expected distortion due to orbital degeneracy
d^1	T_{2g}	small	d^6	$5\,T_{2g}$	small
d^2	$3\,T_{1g}$	small	d^7	$4\,T_{1g}$	small
d^3	$4\,A_{2g}$	0	d^8	$3\,A_{2g}$	0
d^4	$5\,E_g$	large	d^9	$2\,E_g$	large
d^5	$6\,A_{1g}$	0			

When the mechanism of substitution in a series of neighbouring elements is examined by the molecular orbital method [133], it is found that the decisive role is played by the change in antibonding effects in the formation of the activated complex, since the remaining characteristics of the complex either do not change or vary monotonically. This principle can be most usefully illustrated by substitution reactions in octahedral complexes of the type ML_6.

In a dissociative mechanism, the activated complex has the composition ML_5 and the configuration of a tetragonal pyramid (symmetry C_{4v}) or a trigonal bipyramid (symmetry D_{3h}). The change in symmetry and the arrangement of the orbitals in these two cases are shown in Fig. 5.

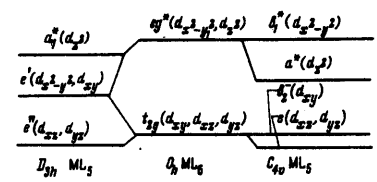

Figure 5. Change in symmetry and arrangement of orbitals for the S_N1 mechanism.

In the formation of ML_5 with the ligands located at the corners of a tetragonal pyramid the non-bonding orbital t_{2g} is converted into the still non-bonding orbitals b_2 and e, while the energy of these orbitals remains fundamentally unchanged. The antibonding orbital e_g is converted into two new antibonding orbitals b_1 and a_1^*, the antibonding effect on the orbitals a_1^* (d_{z^2}) being considerably diminished.

If electrons are present in the e_g^* orbital in a complex, formation of the ML_5 complex should be accompanied by a redistribution of electrons with a gain in energy when they undergo a transition from the orbital e_g^* to the orbital a_1^*. This transition disrupts the monotonic variation in reaction velocity in complexes with metals having d^4, d^5, d^9, and d^{10} configurations (Cr^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Mn^{3+}, etc. complexes), and as a consequence the activation energy is lower, and the rate of substitution reactions higher, for

compounds of these metals than in the case of neighbouring elements. It is probable that substitution by an S_N1 mechanism is typical of compounds of these elements (of the type ML_6).

Similar conclusions can also be reached if the activated complex ML_5 is regarded as a trigonal bipyramid (symmetry D_{3h}). In contrast to the preceding case, substitution in the ML_6 complex of a metal having the electronic structure d^3 (or d^8) should be characterised here by an especially high activation energy, since in these compounds it is necessary to promote one of the electrons from the non-bonding t_{2g} (d_{xy}) orbital to an antibonding orbital e'.

In an associative mechanism (S_N2) the activated complex has the composition ML_7 and the configuration of a pentagonal bipyramid (symmetry D_{5h}) with the characteristic and rearrangement of orbitals shown in Fig. 6. In this case the monotonic change in activation energy (and reaction velocity) breaks down in the complex compounds of metals having the structure d^3 (or d^8) owing to the promotion of one of the electrons from a non-bonding t_{2g} orbital to an antibonding e_2' (d_{xy}) orbital.

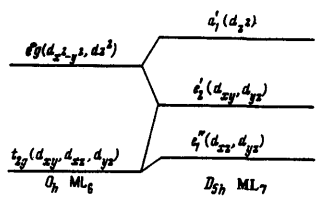

Figure 6. Change in symmetry and arrangement of orbitals for the S_N2 mechanism.

The activation energy is somewhat diminished in the complexes of metals having the configuration $3d^4$ (or $3d^9$), and remains about the same for complexes of metals having the configuration $3d^5$ (or $3d^{10}$) (Table 6).

Table 6. Change in antibonding effect in reactions occurring by S_N1 and S_N2 mechanisms[133].

Electronic structure	σ-Antibonding			π-Antibonding		
	ML_6 (D_{3h})	ML_6 (C_{4v})	ML_7 (D_{5h})	ML_6 (D_{3h})	ML_6 (C_{4v})	ML_7 (D_{5h})
High-spin complexes						
d^1	0.0	0.0	0.0	−0.5	−1.0	+0.5
d^2	0.0	0.0	0.0	−1.0	−2.0	+1.0
d^3	+1.13	0.0	+1.88	−3.5	−2.0	−0.5
d^4	−0.75	−1.0	+0.75	−2.0	−2.0	+2.0
d^5	−1.0	−1.0	+1.0	−2.0	−2.0	+0.5
d^6	−1.0	−1.0	+1.0	−1.5	−3.0	+2.5
d^7	−1.0	−1.0	+1.0	−3.0	−4.0	+3.0
d^8	+0.13	−1.0	+2.88	−5.5	−4.0	+1.5
d^9	−1.75	−2.0	+1.75	−4.0	−4.0	+4.0
Low-spin complexes						
d^3	0.0	0.0	0.0	−1.5	−3.0	+1.5
d^4	0.0	0.0	0.0	−2.0	−4.0	+2.0
d^5	+1.13	0.0	+1.88	−4.0	−4.0	+0.5
d^6	+2.25	0.0	+3.75	−5.5	−4.0	−1.0
d^7	+0.38	−1.0	+2.63	−4.0	−4.0	+1.5
d^8	−1.5	−2.0	+1.5	−4.0	−4.0	+4.0

Experimental results agree well with the variation in rate of substitution by the S_N2 mechanism. Actually, complexes of metals having the electronic configurations d^3 and d^8 react comparatively slowly in substitution reactions, and in this respect differ notably from the complexes of neighbouring metals.

The gradual increase in stability of the complexes with increase in atomic number of the transition metal leads to a gradual increase in the activation energy (decrease in rate) of substitution. This slowing down in the rate becomes especially marked in the complexes of metals having the electronic structures d^3 and d^8 when reactions occur by an S_N2 mechanism, owing to the necessity for promoting one of the electrons to an antibonding orbital. Complexes of metals having d^4, d^5, d^9, and d^{10} configurations, however, are considerably more reactive in an S_N2 and especially in an S_N1 mechanism, because of the transition of one electron from a higher to a lower antibonding orbital.

Unfortunately, none of the available methods enables absolute values to be calculated for the rate constants and activation energies of complex formation. At the best, all existing theories merely explain the relative variation in rate of complex formation in the series of transition elements.

(*b*) Effect of nature of ligand. The rates of many complexing reactions are independent of the nature of the ligands involved. Thus, for example, many doubly charged positive ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) react at approximately the same rate with various ligands (Table 7).

Table 7. Rate constants (in $M^{-1}\,s^{-1}$) for complex formation by the ions Zn^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+} with various ligands*.

Ligand	Ions			
	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
Br^-	$5.0\cdot10^5$	$1.4\cdot10^9$	—	—
I^-	$5\cdot10^5$	$5\cdot10^9$	—	—
SO_4^{2-}	$3\cdot10^6$	$1\cdot10^7$	—	—
dye	$4\cdot10^6$	$1\cdot10^7$	—	—
CH_3COO^-		$3\cdot10^8$	—	—
imid	—	—	$5\cdot10^3$	$1.3\cdot10^5$
gly^-	—	—	$1.5\cdot10^4$	$4.6\cdot10^5$
$dgly^-$	—	—	$2.1\cdot10^4$	$4.6\cdot10^5$
dye	—	—	$4\cdot10^3$	$4.0\cdot10^4$
SO_4^{2-}	—	—	$1\cdot10^4$	$1\cdot10^4$

* imid = imidazole; gly = glycine; dgly = glycylglycine; dye = 2-*p*-dimethylaminophenylazopyridine.

This can be explained by an S_N1 mechanism for these reactions, in conformity with the equations[134]

$$[M(H_2O)_n] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_{n-1}] + H_2O, \qquad (27)$$

$$[M(H_2O)_{n-1}] + L \xrightarrow{k_3} [M(H_2O)_{n-1}L]. \qquad (28)$$

Using the steady-state method and assuming that the concentration of $[M(H_2O)_{n-1}]$ is considerably less than the concentration of $[M(H_2O)_n]$, we can write

$$\frac{d[M(H_2O)_{n-1}L]}{dt} = \frac{k_1k_3[M(H_2O)_n][L]}{k_2+k_3[L]}, \qquad (29)$$

when $k_3 \gg k_2$ we obtain

$$\frac{d[M(H_2O)_{n-1}L]}{dt} = k_1[M(H_2O)_n]. \qquad (30)$$

It follows from Eqn. (30) that the rate-determining stage in the formation of complex compounds is reaction (27)—the

elimination of water—the rate of complex formation being completely independent of the nature of the ligand [134-136] (Table 7).

For the same reason the rate of addition of each successive ligand in stepwise complex formation is usually lower than or equal to the rate of addition of the preceding ligand. If, however, substitution of a water molecule involves intermediate formation of an outer-sphere complex, and its stability constant exceeds unity, the reverse effect may be observed [137,138].

The rate of complex formation is sharply diminished in reactions with polydentate ligands involved in the formation of chelate compounds. This is probably associated with the multistage character of ring formation [135,136,139].

2. Rate of Dissociation of Complexes

The influence of various factors on the rate of dissociation of complexes has been examined in detail by Wilkins and his collaborators [70,137,138,140-144], who showed that the rate of dissociation is more dependent than is the rate of complex formation on the nature of the ligand. Thus, for example, the rate constants for dissociation of the complexes of bivalent nickel—

$$[Ni(CNS)]^{+} \xrightarrow{k_1} Ni^{2+} + CNS^{-}, \quad (31)$$

$$[Ni(NH_3)]^{2+} \xrightarrow{k_2} Ni^{2+} + NH_3, \quad (32)$$

$$[Ni\,(en)]^{2+} \xrightarrow{k_3} Ni^{2+} + en, \quad (33)$$

—are respectively (in s^{-1}) $k_1 = 100$, $k_2 = 5.8$, and $k_3 = 0.14$, whereas the corresponding rate constants for formation of these complexes are 10^4, 10^4, and 10^6 M^{-1} s^{-1}. With many of the reactions described in the literature, dissociation rate constants are always smaller than formation rate constants for the same complex compounds.

If the rate-determining stage in complex formation is the elimination of water, the rule [142]

$$\Delta \lg k_d \approx -\Delta \lg K_{st} \quad (34)$$

where k_d is the dissociation rate constant of the complex compound and K_{st} is the stepwise stability constant of the same compound, holds for complex compounds having the same central ion and different ligands, as well as for individual stages in a multistage process of complex formation. This rule has been verified on a series of compounds of bivalent nickel [142].

3. Influence of Stereochemical Factors

Hardly any work has been done on the influence of stereochemical factors on the rate of fast complex-forming reactions. Data are available only on the dependence of reaction velocity on the angle of attack for ions having different electronic configurations [12,144,145].

Hammes and Steinfeld [and Kustin et al.] [75,139] have found that the rate of formation of complex compounds by bivalent cobalt, nickel, and manganese is considerably lower with β-alanine than with α-alanine. The explanation given [139] for this difference in rates is that ring formation in the above compounds is a stepwise process, while with β-alanine, owing to steric hindrance, occupation of a vacant place by a water molecule is more rapid than closure of the ring. This type of substitution has been termed sterically controlled substitution.

IV. REACTIONS HAVING AN S_N MECHANISM

1. Reactions involving Elements of Group I

Study of the kinetics of complex formation involving alkali-metal ions has been begun only recently. Investigation of these reactions has been delayed for at least two reasons: reactions of complex formation involving the alkali-metal ions occur very rapidly, and the resulting complexes are not very stable, so that all investigations must be conducted with high concentrations of the ligand, when the effect of foreign ions is very considerable. Available published data on these reactions are listed in Table 8.

Table 8. Rate constants in the replacement of water by various ligands for alkali-metal ions* ($\mu = 0.5$, pH > 11, $T = 20°C$).

Ion	Ligands			
	$Edta^{4-}$	Nta^{3-}	$Imda^{2-}$	Tmp^{3-}
Li^+	$4.8 \cdot 10^7$	$4.7 \cdot 10^7$	$2.5 \cdot 10^8$	$9 \cdot 10^8$
Na^+	$4.7 \cdot 10^7$	$8.8 \cdot 10^7$	$2.5 \cdot 10^8$	$2 \cdot 10^9$
K^+	$7.5 \cdot 10^7$	$1.5 \cdot 10^8$	—	$5 \cdot 10^9$
Rb^+	$1.4 \cdot 10^8$	$2.3 \cdot 10^8$	—	$5 \cdot 10^9$
Cs^+	$2.1 \cdot 10^8$	$3.5 \cdot 10^8$	—	$5 \cdot 10^9$

* Constants (in s^{-1}) obtained by the ultrasonic method [14]. $Edta^{4-}$ = ethylenediaminetetra-acetate; Nta^{3-} = nitrilotriacetate anion; $Imda^{2-}$ = imidazole anion; Tmp^{3-} = trimetaphosphate anion.

Table 8 shows that in all cases the rate of complex formation increases monotonically from lithium to caesium, and the rate constant of these processes, which is very large, varies linearly with the radius of the reactant ions [14]. This indicates that the rate of complex formation involving alkali-metal ions depends mainly on the purely electrostatic intereaction of the reactant ions and is controlled by diffusion, the rate of elimination of water not being the limiting stage.

Only reactions involving compounds of bivalent copper have been relatively well studied among elements of subgroup IB. It is seen from Table 9 that the rate constants for formation of one-coordinate complex compounds of bivalent copper with various ligands vary within a fairly narrow range (10^6–10^8 M^{-1} s^{-1}). Such a large absolute value of the rate constant for the formation of complexes of bivalent copper, in comparison with the rate constants for complex formation by other transition elements of the first series, is usually explained by strong distortions of the octahedral structure of copper compounds resulting from the Jahn-Teller effect [6,129,131].

The absence of an appreciable effect of the nature of the ligands on the rate constant of complex formation by bivalent copper is probably associated with the fact that these reactions occur by an S_N1 mechanism, the rate-determining stage being the elimination of water [13,14].

The literature contains no data on fast complexing reactions involving compounds of silver, gold, or univalent and tervalent copper.

Table 9. Rate constants for the formation and the dissociation of complex compounds of bivalent copper*;

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$[Cu(H_2\overset{*}{O})_6]^{2+} + H_2O \rightleftarrows [Cu(H_2O)_6]^{2+} + H_2\overset{*}{O}$	$3\cdot10^8$	—	25°	n.m.r.	134,146,1
$[Cu(\overset{*}{NH_3})]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)]^{2+} + \overset{*}{NH_3}$	$7\cdot10^6$	--	25°	n.m.r.	148
$[Cu(en)_2(H_2O)_2]^{2+} + en \rightleftarrows [Cu(en)_2(H_2O)_2]^{2+} + en$	—	$2.4\cdot10^7$	27°	n.m.r.	149
$Cu^{2+} + SO_4^{2-} \rightleftarrows [Cu(SO_4)]$	$5\cdot10^7$	10^8	25°	us	150,1
$Cu^{2+} + CH_3COO^- \rightleftarrows [Cu(CH_3COO)]^+$	$4.3\cdot10^8$		25°	n.m.r.	146
$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+}$	$6.6\cdot10^4$	$1.9\cdot10^7$	27°	n.m.r.	115
$[Cu(NH_3)_4]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_5]^{2+}$	$5.7\cdot10^6$	—	27°	n.m.r.	115
$[Cu(NH_3)_5]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_6]^{2+}$	$6.6\cdot10^4$	—	25°	n.m.r.	152
$Cu^{2+} + en \rightleftarrows [Cu(en)]^{2+}$	115	—	25°	stfl	70
$[Cu(en)]^{2+} + en \rightleftarrows [Cu(en)_2]^{2+}$	433	—	0.15 M HNO_3 25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + Edta^{4-} \rightleftarrows [Cu(Edta)]^{2-}$	370	$1.3\cdot10^9$	0°, $\mu = 0.1$	elch	154,155
$Cu^{2+} + dye \rightleftarrows [Cu(dye)]^{2+}$	—	$1\cdot10^8$	15° 0.1 M KNO_3	tj	146
$[Cu(sarc)]^+ + sarc^- \rightleftarrows [Cu(sarc)_2]$	—	$6\cdot10^5$	27°	n.m.r.	115
$[Cu(dmg)]^+ + dmg^- \rightleftarrows [Cu(dmg)_2]$	—	$1.3\cdot10^4$	27°	n.m.r.	115
$[Cu(gly)]^+ + gly^- \rightleftarrows [Cu(gly)_2]$	—	$8.2\cdot10^6$	27°	n.m.r.	115
$Cu^{2+} + bn \rightleftarrows [Cu(bn)]^{2+}$	4.56	—	25°	stfl	70
$[Cu(bn)]^{2+} + bn \rightleftarrows [Cu(bn)_2]^{2+}$	15.1	—	25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + C\text{-tetraM} \rightleftarrows [Cu(C\text{-tetraM})]^{2+}$	0.42	—	25° 0.15 M HNO_3	stfl	70
$[Cu(C\text{-tetra M})]^{2+} + C\text{-tetra M} \rightleftarrows [Cu(C\text{-tetra M})_2]^{2+}$	0.80	—	25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + terpy \rightleftarrows [Cu(terpy)]^{2+}$		$2\cdot10^7$	5°	stfl	137

* en = ethylenediamine; Edta = ethylenediaminetetra-acetate; dye = 2-*p*-dimethylaminophenylazopyridine; bn = butane-2,3-diamine; gly = glycine; sarc = *N*-methylglycine; dmg = *NN*-dimethylglycine; C-tetraM = 2,3-dimethylbutane-2,3-diamine; n.m.r. = nuclear magnetic resonance method; us = ultrasonic method; stfl = stopped-flow method; elch = electrochemical method; tj = temperature-jump relaxation method.

Table 10. Rate constants for the formation and the dissociation of complex compounds of Group II elements.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$[Be(H_2\overset{*}{O})_n]^{2+} + H_2O \rightleftarrows [Be(H_2O)_n]^{2+} + H_2\overset{*}{O}$	10^2	—		us	14
$[Be(H_2O)SO_4] \rightleftarrows [Be(SO_4)] + H_2O$ **	$1.3\cdot10^3$	$1\cdot10^3$	12° 0.01 0.01–0.2 M $BeSO_4$	tj ps	78,155 156
$[Mg(H_2O)_n]^{2+} + H_2O \rightleftarrows [Mg(H_2O)_n]^{2+} + H_2O$	10^5	—		us	14
$[Mg(H_2O)SO_4] \rightleftarrows [Mg(SO_4)] + H_2O$ **	$8\cdot10^5$	$1\cdot10^5$		tj	78
$Mg^{2+} + SO_4^{2-} \rightleftarrows [Mg(SO_4)]$	$5.52\cdot10^5$ $6.47\cdot10^5$	$8.76\cdot10^7$ $10.3\cdot10^7$	12° 0.003 0.003–0.2 M $MgSO_4$	tj us	78 97,101
$[Mg(H_2O)S_2O_3] \rightleftarrows [Mg(S_2O_3)] + H_2O$**	$1\cdot10^6$	10^5		tj	78
$[Mg(H_2O)CrO_4] \rightleftarrows [MgCrO_4] + H_2O$ **	$1.5\cdot10^6$	10^5		tj	78
$Mg^{2+} + ADP^{3-} \rightleftarrows MgADP^-$	$2.5\cdot10^3$	$3\cdot10^6$	13°	tj	158
$[Ca(H_2\overset{*}{O})_n]^{2+} + H_2O \rightleftarrows [Ca(H_2O)_n]^{2+} + H_2\overset{*}{O}$	10^8	—		us	14
$Mg^{2+} + HT^{3-} \rightleftarrows MgHT^-$	$3.0\cdot10^4$	$3.5\cdot10^6$	pH=9	tj	159
$[Ca(H_2O)CrO_4] \rightleftarrows [Ca(CrO_4)] + H_2O$	$2\cdot10^8$	$2\cdot10^7$		tj	78
$Ca^{2+} + X_o^{2-} \rightleftarrows CaX_o$	—	$7\cdot10^8$		tj	79
$Mg^{2+} + X_o^{2-} \rightleftarrows MgX_o$	—	$1.6\cdot10^6$		tj	79
$[Sr(H_2O)_n]^{2+} + H_2O \rightleftarrows [Sr(H_2O)_n]^{2+} + H_2\overset{*}{O}$	$2\cdot10^8$	—		us	14
$[Ba(H_2\overset{*}{O})_n]^{2+} + H_2O \rightleftarrows [Ba(H_2O)_n]^{2+} + H_2\overset{*}{O}$	$2.5\cdot10^9$	—		us	14

** Reactions of conversion of outer-sphere into inner-sphere complexes (k_{form} in s^{-1}).

ADP^{3-} = adenosine 5-diphosphate; HT^{3-} = Tiron [disodium 4,5-dihydroxybenzene-1,3-disulphonate]; X_o = Xylenol Orange; us = ultrasonic method; tj = temperature-jump relaxation method; ps = pressure-shock method.

2. Reactions Involving Elements of Group II

Available published values of the rate constants for the dissociation and the formation of complexes of Group II elements are given in Table 10. The rates of all these reactions, with the exception of those involving beryllium, are determined purely by electrostatic interaction, the elimination of water being the rate-determining stage. It is interesting that the rate of complex formation increases sharply on passing from magnesium to calcium, a fact which has not yet been satisfactorily explained[14].

The relatively small rate constant found with beryllium ions is explained by rapid hydrolysis, as a result of which relatively unreactive species are formed[14,151]. These processes can explain the presence of at least six relaxation times in the relaxation spectrum of beryllium sulphate[151].

Subgroup IIB contains elements whose ions have the configuration d^{10}. In contrast to the alkaline-earth ions, the doubly charged ions of zinc, cadmium, and mercury have an outer d-shell, which may be reflected in their kinetic properties. The comparatively high velocities of reactions involving ions of these elements (Table 11), whose rate constants are approximately equal in magnitude to those of reactions involving elements of the A subgroup, suggest that the mechanism of complex formation is the same in both cases, the rate of the process being determined purely by electrostatic interaction and being limited by diffusion.

3. Reactions Involving Elements of Groups III–VI and Manganese

Preliminary results indicate[14] that complex formation involving V^{2+} ions is abnormally slow, but the ion Cr^{2+} reacts at approximately the same rate as does Cu^{2+}. These data are consistent with the ligand field theory.

Complex formation involving compounds of bivalent manganese is very rapid. Quantitative kinetic data are available for the exchange of water in the inner sphere[111,148] and the formation of sulphate complexes[101] and of complexes with terpyridyl[137] and β-alanine[139]. In most cases the rate constant for the formation of bivalent manganese complexes exceeds $10^6\ M^{-1}\ s^{-1}$.

Fast complexing reactions in which ions of elements in these groups take part in a higher state of oxidation than 3 have not been investigated. Data are available only on the rate of formation of sulphate complexes of aluminium[157] and vanadyl[97] and of dimers of tungsten(VI) and molybdenum(VI).[165]

Few data are available also on reactions involving ions of the rare-earth elements. Eigen[14] assumes that the rate constant for complex formation should be of the order of $10^7\ M^{-1}\ s^{-1}$. This supposition is supported by results for the exchange of ethylenediaminetetra-acetic acid with certain rare-earth ions[166]. For lanthanum this constant is $10^5\ M^{-1}\ s^{-1}$, and it decreases in the sequence—lanthanum, neodymium, dysprosium, ytterbium—in the proportions 7700 : 1200 : 19 : 1.

The temperature-jump method[167] has recently been used to determine the rate constants for the formation and the dissociation of the complexes of lanthanides with murexide,

Table 11. Rate constants of complex formation by elements in Subgroup IIB*.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$Zn^{2+} + Br^- \rightleftarrows ZnBr^+$	$\leqslant 5\cdot10^8$	$5.0\cdot10^8$	25°	n.m.r.	160
$ZnBr^+ + Br^- \rightleftarrows ZnBr_2$	—	$5.0\cdot10^5$	0.01-5.0 M NaBr	n.m.r.	160
$ZnBr_2 + Br^- \rightleftarrows ZnBr_3^-$	$\geqslant 7\cdot10^6$	$5.0\cdot10^5$	ditto	n.m.r.	160
$ZnBr_3^- + Br^- \rightleftarrows ZnBr_4^{2-}$	$2.0\cdot10^7$	$8\cdot10^7$	»	n.m.r.	160
$Zn^{2+} + I^- \rightleftarrows ZnI^+$	$5\cdot10^4$	$5\cdot10^5$	25° 0.01-5.0 M KI	n.m.r.	160
$ZnI^+ + I^- \rightleftarrows ZnI_2$	—	$5\cdot10^5$	ditto	n.m.r.	160
$ZnI_2 + I^- \rightleftarrows ZnI_3^-$	$\leqslant 5\cdot10^4$	$5\cdot10^5$	»	n.m.r.	160
$ZnI_3^- + I^- \rightleftarrows ZnI_4^{2-}$	$3\cdot10^7$	$7\cdot10^6$	»	n.m.r.	160
$ZnF^+ + F^- \rightleftarrows ZnF_2$		$\tau \geqslant 10^{-4}$		n.m.r.	160
$Zn^{2+} + SO_4^{2-} \rightleftarrows ZnSO_4$	$>10^8$	$3\cdot10^6$	25°	n.m.r.	146
		10^7		tj	78
$Zn^{2+} + CH_3COO^- \rightleftarrows ZnCH_3COO^-$	$3\cdot10^7$	—	25°	n.m.r.	146
$Zn^{2+} + dye \rightleftarrows [Zn\,(dye)]^{2+}$	—	$4\cdot10^6$	15° 0.1 M KNO_3	tj	146
$Zn^{2+} + terpy \rightleftarrows [Zn\,(terpy)]^{2+}$	1,1	$1.3\cdot10^6$	25°	stfl	137
$CdCl_3^- + Cl^- \rightleftarrows CdCl_4^{2-}$	$7.6\cdot10^9$	$4\cdot10^9$	25°	us	106
$Cd^{2+} + Br^- \rightleftarrows CdBr^+$	$1.0\cdot10^7$	$1.4\cdot10^7$	25° 0.01-5.0 M NaBr	n.m.r.	160
$CdBr^+ + Br^- \rightleftarrows CdBr_2$	$1.4\cdot10^6$	$1.4\cdot10^8$	ditto	n.m.r.	160
$CdBr_2 + Br^- \rightleftarrows CdBr_3^-$	$7\cdot10^6$	$1.7\cdot10^7$	»	n.m.r.	160
$CdBr_3^- + Br^- \rightleftarrows CdBr_4^{2-}$	$6.0\cdot10^6$	$1.2\cdot10^7$	»	n.m.r.	160
$Cd^{2+} + I^- \rightleftarrows CdI^+$	$\approx 2\cdot10^7$	$\approx 5\cdot10^9$	25° 0.01-5.0 M KI	n.m.r.	160
$CdI_3^- + I^- \rightleftarrows CdI_4^{2-}$	$\approx 2\cdot10^7$	$\approx 5\cdot10^8$	ditto	n.m.r.	160
$Cd^{2+} + SO_4^{2-} \rightleftarrows CdSO_4$	10^8	10^7	0.1 M KNO_3	tj	78
$[Cd\,(CN)]^+ + CN^- \rightleftarrows [Cd\,(CN)_2]$	—	$5\cdot10^8$	$\mu = 0.1$	elch	161
$[Cd\,(CN)_2] + CN^- \rightleftarrows [Cd\,(CN)]^-$	$2.7\cdot10^8$	$4\cdot10^{11}$	ditto	elch	162
$[Cd\,(CN)_3]^- + CN^- \rightleftarrows [Cd\,(CN)_4]^{2-}$	$2\cdot10^4$	$8\cdot10^7$	3 M $NaClO_4$	elch	163
$Cd^{2+} + CH_3COO^- \rightleftarrows [Cd\,(CH_3COO)]^+$	—	$3\cdot10^8$		n.m.r.	137
$Cd^{2+} + dye \rightleftarrows [Cd\,(dye)]^{2+}$	—	10^7	15° 0.1 M KNO_3	tj	146
$Cd^{2+} + terpy \rightleftarrows [Cd\,(terpy)]^{2+}$	25	$3.2\cdot10^6$	25°	stfl	137
$HgCl^+ + Cl^- \rightleftarrows HgCl_2$	$2.5\cdot10^7$	$6.4\cdot10^9$		n.m.r.	160
$HgBr_2 + Br^- \rightleftarrows [HgBr_3]^-$	$2.5\cdot10^7$	$4.6\cdot10^8$	25° 0.01-5.0 M NaBr	n.m.r.	160
$[HgBr_3]^- + Br^- \rightleftarrows [HgBr_4]^{2-}$	—	$5\cdot10^9$	ditto	efp	164

* dye = 2-*p*-dimethylaminophenylazopyridine; terpy = 2,2′,6′,2″-terpyridyl; n.m.r. = nuclear magnetic resonance method; tj = temperature-jump method; efp = electric field-pulse method; elch = electrochemical method; us = ultrasonic method; stfl = stopped-flow method.

and the stopped-flow method to find the dissociation rate constants of the complexes formed by Xylenol Orange with the rare-earth elements of the cerium subgroup[168] (see Table 12). It is possible that, in aqueous solutions of compounds of the rare-earth elements, an equilibrium is established between hydrated forms containing different quantities of water in the inner sphere, and that these forms differ in reactivity[167].

4. Reactions Involving Elements of the Ion Group

Data on fast reactions of complex formation involving elements of this group are the most numerous (Table 13). In most cases the rate of complex formation is limited by the rate of elimination of water from the inner sphere, and is therefore independent of the nature of the ligand.

Two groups of reactions occur with Fe^{3+} ions. The first group comprises reactions in which a ligand reacts directly

Table 12. Rate constants for the reaction $M^{3+} + L^n \rightleftharpoons ML^{3-n}$, where M^{3+} is a lanthanide ion and L^n represents murexide or Zylenol Orange.

L	M^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
* Mur	$10^3 k_{diss}$, s^{-1}	32	21	24	8.5	6.5	5.5	4,3
* Mur	$10^7 k_{form}$, $M^{-1}\,s^{-1}$	8.6	9.5	8.6	9.3	9.6	8.2	5.2
X_o	k_{diss}, s^{-1}	152	236	159	116	106	—	95
	M^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
* Mur	$10^3 k_{diss}$, s^{-1}	3.3	2.8	3.3	3.4	5.0	4.3	4.5
Mur	$10^7 k_{form}$, $M^{-1}\,s^{-1}$	3.0	1.7	1.4	1.0	1.1	1.1	1.3

* Mur = murexide, $\mu = 0.1$, $T = 12°C$, pH = 4.0; X_o = Xylenol Orange, $T = 25°C$, pH = 4.90.

with the ions according to the equation

$$Fe^{3+} + X^- \xrightarrow{k_1} FeX^{2+} . \qquad (35)$$

Reactions of the second group occur in conformity with the scheme

$$FeOH^{2+} + HX \xrightarrow{k_1} FeX^{2+} + H_2O \qquad (36)$$

As is evident from Eqn. (35), in the former case k is independent of the hydrogen-ion concentration, whereas the rate constant of reaction (36) is substantially influenced by it. As a rule $k_2 \gg k_1$. In many cases the dissociation of complex compounds of tervalent iron is catalysed by Fe^{2+} ions[72].

The Ni^{2+} ion, which has the electronic configuration d^8 and forms highly symmetrical complex compounds, reacts considerably more slowly than the other transition elements of the first series.

The literature contains no data on fast reactions of complex formation by elements of the platinum group.

V. REACTIONS HAVING AN S_E MECHANISM

Substitution of the central ion in complex compounds has so far been studied mainly on slow or moderately rapid[189-191] reactions in which polydentate ligands take part.

The most interesting of the reactions which have been studied is

$$NiTeta^{2+} + CuEdta^{2-} \rightleftarrows CuTeta^{2+} + NiEdta^{2-} , \qquad (37)$$

where Teta represents triethylenetetra-amine and Edta represents ethylenediaminetetra-acetic acid. This reaction—the first non-redox reaction to be studied—has been shown[192] to have a chain mechanism, which can be represented by the reactions

$$NiTeta^{2+} \rightleftarrows Ni^{2+} + Teta , \qquad (38)$$

$$Teta + CuEdta^{2} \rightleftarrows CuTeta^{2+} + Edta^{4-} , \qquad (39)$$

$$Edta^{4-} + NiTeta^{2+} \rightleftarrows NiEdta^{2-} + Teta , \qquad (40)$$

$$Ni^{2+} + Edta^{4-} \rightleftarrows NiEdta^{2-} . \qquad (41)$$

It is interesting that this reaction is catalysed by small amounts (10^{-6} M) of certain ligands (Teta, Edta), and is inhibited by copper and nickel ions at concentrations of

Table 13. Rate constants of fast complex formation by elements of the iron group.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
1	2	3	4	5	6
$[Fe(H_2O)_n]^{3+} + H_2O \rightleftarrows [Fe(H_2O)_n]^{3+} + H_2O$	$2.4\cdot10^4$	—		n.m.r.	148
$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4$	10^6	$6\cdot10^6$		tj	78
$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$ **	$k_1=1.1$ $k_2=3.4$	$1.9\cdot10^2$	25°; $\mu=3.0$	n.m.r	148
	$k_1=9.4$ $k_2=18$		25°; $\mu=1.0$ Fe^{2+} catalyst	stfl	65,72
$Fe^{3+} + CNS^- \rightleftarrows FeCNS^{2+}$	—	$1.7\cdot10^4$ $k_1=127$ $k_2=20$	20°; $\mu=0.01$	stfl	71,169 170
		132	25°	tj	171
$Fe^{3+} + Br^- \rightleftarrows FeBr^{2+}$	—	20		stfl	172,173
$Fe^{3+} + Fe^- \rightleftarrows FeF^{2+}$		$5.0\cdot10^3$		stfl	172,174
$Fe^{3+} + N_3^- \rightleftarrows FeN_3^{2+}$	—	$1.6\cdot10^5$		stfl	172
$Fe^{3+} + CNS^- \rightleftarrows FeCNS^{2+}$ **	$k_1=0.28$ $k_2=0.016$	—	80% CH_3OH 20% H_2O −45°	stfl	175
$FeOH^{2+} + HCl \rightleftarrows FeCl^{2+} + H_2O$	—	$1.1\cdot10^4$	25°	stfl	158
		18		stfl	65
$FeOH^{2+} + HBr \rightleftarrows FeBr^{2+} + H_2O$	—	$2.7\cdot10^4$		stfl	172,173
$FeOH^{2+} + HF \rightleftarrows FeF^{2+} + H_2O$	—	$3.1\cdot10^3$		stfl	172,174
$FeOH^{2+} + HN_3 \rightleftarrows FeN_3^{2+} + H_2O$	—	$6.8\cdot10^3$		stfl	172
$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4^+$	$6.3\cdot10^4$	$6.4\cdot10^3$	25°; $\mu=0.5$	cfl	176,177
$FeOH^{2+} + HCNS \rightleftarrows FeCNS^{2+} + H_2O$	20.2	$1.0\cdot10^4$		stfl	170,172
$FeOH^{2+} + HSO_4^- \rightleftarrows FeSO_4^+ + H_2O$	—	$3\cdot10^5$		cfl	176
$[Fe(H_2O)OH]^{2+} + Cl^- \rightleftarrows [Fe(H_2O)(OH)Cl]^+$	—	$1.1\cdot10^4$	25°; $\mu=1.0$	stfl	65
$FeOH^{2+} + CNS^- \rightleftarrows [Fe(OH)CNS]^+$	—	$4.2\cdot10^4$	25°	tj	171
$Fe(OH)^{2+} + Fe(OH)^{2+} \rightleftarrows [Fe(OH)_2Fe]^{4+}$	1.0	450	24.5°; $\mu=0.3$	stfl	173,178
$FeCl^{2+} + Fe(OH)^{2+} \rightleftarrows [Fe(OH)ClFe]^{4+}$	—	100	ditto	ps	178
$Fe(OH)^{2+} + FeCNS^{2+} \rightleftarrows [Fe(OH)CNSFe]^{4+}$	—	85	»	ps	178
$FeSO_4^+ + Fe(OH)^{2+} \rightleftarrows [Fe(OH)SO_4Fe]^{3+}$	—	110	ditto	ps	178
$Fe^{3+} + S_2O_3^{2-} \rightleftarrows [Fe(S_2O_3)]^+$				cfl	179
$Fe^{3+} + terpy \rightleftarrows [Fe(terpy)]^{3+}$	$6.3\cdot10^{-8}$	$8.0\cdot10^4$	25°	stfl	137
$[Fe(terpy)]^{3+} + terpy \rightleftarrows [Fe(terpy)_2]^{3+}$	$8.0\cdot10^{-7}$	10^7	5°	stfl	137
$Co^{2+} + SO_4^{2-} \rightleftarrows CoSO_4$	$> 10^7$	10^3		tj	78
		$2\cdot10^5$		n.m.r.	148
$[Co(H_2O)_6]^{2+} + H_2O \rightleftarrows [Co(H_2O)_6]^{2+} + H_2O$	$3.1\cdot10^5$	—		n.m.r.	148,115
$[Co(H_2O)_6]^{2+} + Cl^- \rightleftarrows [Co(H_2O)_5Cl]^{2+} + H_2O$	0.05	2	25°; $\mu=3.0$	stfl	180,181
$[Co(H_2O)_5OH]^{2+} + Cl^- \rightleftarrows [Co(H_2O)_4(OH)Cl]^+ + H_2O$	—	$2\cdot10^2$	25°; $\mu=3.0$	stfl	181
$[Co(NH_3)_5]^{3+} + NH_3 \rightleftarrows [Co(NH_3)_5]^{3+} + NH_3$	$4.7\cdot10^4$	—	25°	n.m.r.	115
$[Co(en)_3]^{3+} + en \rightleftarrows [Co(en)_3]^{3+} + en$	$4.8\cdot10^3$	—	25°	n.m.r.	115
$Co^{2+} + dye \rightleftarrows [Co(dye)]^{2+}$	—	$4.0\cdot10^4$	15°; $\mu=0.1$	tj	146
$Co^{2+} + HT^{3-} \rightleftarrows CoHT^-$	$4.2\cdot10^3$	$4.0\cdot10^6$		tj	159
$Co^{2+} + gly \rightleftarrows [Co(gly)]^+$	10	$4.6\cdot10^5$	25°, $\mu=0.10$, pH 9.0–9.5	tj	75
$[Co(gly)]^+ + gly^- \rightleftarrows [Co(gly)_2]$	360	$4.6\cdot10^5$	ditto	tj	75
$[Co(gly)_2] + gly^- \rightleftarrows [Co(gly)_3]^-$	$3.8\cdot10^2$	$9.0\cdot10^5$	»	tj	75
$Co^{2+} + dgly \rightleftarrows [Co(dgly)]^+$	$4.2\cdot10^2$	$4.6\cdot10^5$	25°, $\mu=0.15$ pH 7.7–8.2	tj	75
$[Co(dgly)]^+ + dgly^- \rightleftarrows [Co(dgly)_2]$	$4.8\cdot10^2$	$9.0\cdot10^5$	ditto	tj	75
$Co^{2+} + imid \rightleftarrows [Co(imid)]^{2+}$	$4.6\cdot10^5$	$1.3\cdot10^5$	25°, $\mu=0.15$, pH 7.1–7.5	tj	75
$[Co(imid)]^{2+} + imid \rightleftarrows [Co(imid)_2]^{2+}$	$9.0\cdot10^4$	$1.1\cdot10^5$	ditto	tj	75
$Co^{2+} + terpy \rightleftarrows [Co(terpy)]^{2+}$	10^{-4}	$2.5\cdot10^4$	25°	stfl	137
$Co^{2+} + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})]^+$	32	$6.0\cdot10^5$	20°, $\mu=0.1$, pH=9.0	tj	139
$[Co(\alpha\text{-alan})]^+ + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})_2]$	280	$8.0\cdot10^5$	ditto	tj	139
$[Co(\alpha\text{-alan})_2] + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})_3]^-$	$1.6\cdot10^3$	$9.0\cdot10^4$	»	tj	139
$Co^{2+} + \beta\text{-alan}^- \rightleftarrows [Co(\beta\text{-alan})]^+$	7,5	$7.5\cdot10^4$	20°, $\mu=0.1$, pH=8.5	tj	139
$[Co(\beta\text{-alan})]^+ + \beta\text{-alan}^- \rightleftarrows [Co(\beta\text{-alan})_2]$	86	$8.6\cdot10^4$	ditto	tj	139
$[Ni(H_2O)_6]^{2+} + H_2O \rightleftarrows [Ni(H_2O)_6]^{2+} + H_2O$	$3.2\cdot10^4$ $4.4\cdot10^3$	—		n.m.r. n.m.r.	148 115
$Ni^{2+} + CNS^- \rightleftarrows [Ni(CNS)]^+$	10^2	$3.5\cdot10^2$	25°, $\mu=0.5$	stfl	152
		$1.8\cdot10^3$	ditto	n.m.r. elch	182,183
$[Ni(CNS)]^+ + CNS^- \rightleftarrows [Ni(CNS)_2]$	—	$3.8\cdot10^3$		elch	182,183
		$6.3\cdot10^4$		elch	182,183
$[Ni(H_2O)_2(CNS)_4]^{2-} + CNS^- \rightleftarrows [Ni(H_2O)_2(CNS)_4]^{3+} + CNS^-$	$6.9\cdot10^5$	—	25°, $\mu=8.4$	n.m.r.	184

Table 13. (cont'd)

1	2	3	4	5	6
$Ni^{2+} + NH_3 \rightleftarrows [Ni(NH_3)]^{2+}$	6.0	—	25°	n.m.r.	184
	0.011	—	−25°	stfl lt	185
				stfl	185
$[Ni(NH_3)_5]^{2+} + NH_3 \rightleftarrows [Ni(NH_3)_6]^{2+}$	$6.6\cdot10^4$	—	25°	n.m.r.	152
$[Ni(NH_3)_6]^{2+} + NH_3 \rightleftarrows [Ni(NH_3)_6]^{3+} + NH_3$	$5.6\cdot10^4$ $4.5\cdot10^4$	— $\tau=0.025$	25° −50°	n.m.r. n.m.r. stfl	186 115 187
$Ni^{2+} + en \rightleftarrows [Ni(en)]^{2+}$	0.15	$9\cdot10^6$	25°	stfl	141,142,143
$[Ni(en)]^{2+} + en \rightleftarrows [Ni(en)_2]^{2+}$	5.2	$1.6\cdot10^6$	25°	stfl	141,142,143
$[Ni(en)_2]^{2+} + en \rightleftarrows [Ni(en)_3]^{2+}$	87	$6\cdot10^6$	25°	stfl	141,142,143
$Ni^{2+} + SO_4^{2-} \rightleftarrows [Ni(SO_4)]$	$1.5\cdot10^4$	$1.0\cdot10^4$		n.m.r.	146,148
		$1.0\cdot10^5$		tj	78
$Ni^{2+} + bn \rightleftarrows [Ni(bn)]^{2+}$	0,020		25°	stfl	142,141
$Ni(bn)]^{2+} + bn \rightleftarrows [Ni(bn)_2]^{2+}$	0.26	—	25°	stfl	141,142
$[Ni(bn)_2]^{2+} + bn \rightleftarrows [Ni(bn)_3]^{2+}$	8.25	—	25°	stfl	141,142
$Ni^{2+} + py \rightleftarrows [Ni(py)]^{2+}$	39	$8.1\cdot10^5$	25°, $\mu=0.1$	elch	183
$Ni(py)]^{2+} py \rightleftarrows [Ni(py)_2]^{2+}$	—	$4.4\cdot10^3$	25°, $\mu=1.0$	stfl elch	144 183
$Ni^{2+} + C_2H_4NH \rightleftarrows [Ni(C_2H_4NH)]^{2+}$	5.0	—		stfl	185
$Ni^{2+} + N_2H_4 \rightleftarrows [Ni(N_2H_4)]^{2+}$	3.6			stfl	185
$Ni^{2+} + gly \rightleftarrows [Ni(gly)]^+$	0.024	$1,5\cdot10^4$	25°, $\mu=0.15$, pH 9.0–9.8	tj	75
$[Ni(gly)]^+ + gly^- \rightleftarrows [Ni(gly)_2]$	0.95	$6.0\cdot10^4$	ditto	tj	75
$[Ni(gly)_2] + gly \rightleftarrows [Ni(gly)_3]^-$	10.4	$4.2\cdot10^4$	»	tj	75
$Ni^{2+} + dgly^- \rightleftarrows [Ni(dgly)]^+$	2.6	$2.1\cdot10^4$	25°, $\mu=0.15$, pH 7.7–8.2	tj	75
$[Ni(dgly)]^+ + dgly^- \rightleftarrows [Ni(dgly)_2]$	2.0	$4.0\cdot10^3$	ditto	tj	75
$[Ni(dgly)_2] + dgly^- \rightleftarrows [Ni(dgly)_3]^-$	32	$3.3\cdot10^3$	»	tj	75
Ni^{2+} imid $\rightleftarrows$ [Ni (imid)]$^{2+}$	2.7	$5.0\cdot10^3$	25°, $\mu=0.15$, pH = 7.1	tj	75
$[Ni(imid)]^{2+} + imid \rightleftarrows [Ni(imid)_2]^{2+}$	8.9	$4.3\cdot10^3$	ditto	tj	75
$[Ni(imid)_2]^{2+} + imid \rightleftarrows [Ni(imid)_3]^{2+}$	17	$2.4\cdot10^3$	»	tj	75
$Ni^{2+} + dye \rightleftarrows [Ni(dye)]^{2+}$	—	$4\cdot10^3$		tj	146
$Ni^{2+} + HT^{3-} \rightleftarrows NiHT^-$	$2.8\cdot10^2$	$2.9\cdot10^5$	15°	tj	159
$Ni^{2+} + C_2O_4^{2-} \rightleftarrows NiC_2O_4$	3.6	$7.5\cdot10^4$	25°, $\mu=0.1$	stfl	186
$Ni^{2+} + HC_2O_4^- \rightleftarrows NiC_2O_4 + H^+$ *	$1.5\cdot10^3$	$5\cdot10^3$	ditto	stfl	186
$[Ni(H_2O_6)]^{2+} + Mal^{2-} \rightleftarrows [(H_2O)_4NiMal]$	42	$4.2\cdot10^5$	25°, $\mu=0,0$	ps	188
$Ni^{2+} + terpy \rightleftarrows [Ni(terpy)]^{2+}$	$2.5\cdot10^{-8}$	$1,3\cdot10^3$	25	stfl	137
$[Ni(terpy)]^{2+} + terpy \rightleftarrows [Ni(terpy)]^{2+}$	$1.6\cdot10^{-6}$	$2,0\cdot10^5$	25	stfl	137
$Ni^{2+} + \alpha\text{-alan}^- \rightleftarrows [Ni(\alpha\text{-alan})]^+$	0.022	$2\cdot10^4$	20°, $\mu=0.1$	tj	139
$[Ni(\alpha\text{-alan})]^+ + \alpha\text{-alan}^- \rightleftarrows [Ni(\alpha\text{-alan})_2]$	0.80	$4\cdot10^4$	ditto	tj	139
$Ni^{2+} + \beta\text{-alan}^- \rightleftarrows [Ni(\beta\text{-alan})]^+$	0.23	$1.0\cdot10^4$	»	tj	139
$[Ni(\beta\text{-alan})]^+ + \beta\text{-alan}^- \rightleftarrows [Ni(\beta\text{-alan})]_2$	27	$6.9\cdot10^3$	»	tj	139

* Dimensions $M^{-1}\,s^{-1}$.

Symbols: en = ethylenediamine; dye = 2-*p*-dimethylaminophenylazopyridine; HT^{3-} = Tiron; gly = glycine; dgly = glycylglycine; imid = imidazole; py = pyridine; bn = butane-2,3-diamine; C_2N_4NH = aziridine; N_2H_4 = hydrazine; α-alan = α-alanine; β-alan = β-alanine; terpy = 2,2′,6′,2″-terpyridyl; Mal = malonate.

** $k = k_1 + k_2/[H^+]$.

Methods: cfl = constant flow; stfl = stopped flow; tj = temperature jump; ps = pressure shock; lt = low-temperature method; n.m.r. = nuclear magnetic resonance method; elch = electrochemical method.

10^{-6} M, which may be utilised for the quantitative determination of these substances.

The above facts are worthy of attention, since many reactions of complex formation occurring by an S_E mechanism are probably chain reactions, as Margerum has shown for several processes analogous to reaction (37). [193,194]

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Influence of Intermolecular and Intramolecular Order on the Infrared Absorption Spectra of Polymers

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In the investigation of the vibrational spectra of macromolecular compounds it has been noticed that, when a polymer passes from the amorphous to the crystalline state, new absorption bands appear in the spectrum, or else splitting occurs in bands present in the spectrum of the amorphous substance. With certain polymers it has been established that several bands increase in intensity on passage from the crystalline to the amorphous state. The former group have been termed "crystalline" bands, and the second group "amorphous" bands. The origin of these absorption bands will become clear from a general theoretical examination of the vibrations described by an individual polymer chain and the crystalline unit cell formed by the chains. The method of theoretical examination of the normal vibrations of the crystalline polymer[1-5] is based on the application of group theory and is analogous to the method employed to investigate the vibrations of molecular crystals[6-8]. In a crystalline polymer the potential field of the crystal acts on the molecule in the same way as in molecular crystals. This should lead to a change in the spectrum of the crystalline polymer as compared with the amorphous material. Certain types of vibrations, which are inactive in an individual polymer molecule, may be active in the unit cell of a three-dimensional or one-dimensional crystal, since the symmetry of a molecule in a crystal field is usually lower than the symmetry of a free molecule. This results in a weakening of the selection rules found for an isolated molecule. It must be noted that, if degenerate vibrations occurred in an isolated molecule, the change in selection rules might result in elimination of the degeneracy. The appearance of "crystalline" bands also may be due to a change in the configuration of the molecular chain in the crystal cell of the polymer compared with its configuration in the amorphous state. Consideration of the vibration of an individual molecule in the crystal field is not complete, since it takes no account of the interactions of vibrations between chains in the crystal cell. This can be done in a theoretical investigation of vibrations in the unit cell of a crystal as a whole.

In the spectra of many polymers, transition from the amorphous to the crystalline state is accompanied not only by weakening of the selection rules but also by splitting of the main vibration frequencies. Physically such splitting occurs as a result of the resonance interaction of analogous vibrations undergone by individual chains in the unit cell. If n molecules are contained in the unit cell, as a result of resonance interaction, there will be n vibrations corresponding to each undegenerate vibration of an isolated molecule. The magnitude of the resonance splitting of frequencies will depend on the intermolecular interaction; it may be so small as to be unobservable experimentally. Furthermore, not all components of the resolved band are active in the infrared absorption spectrum.

Considerable interest attaches to study of the vibrational spectra of polymers having a regular chain structure (isotactic and syndiotactic polymers). In several cases these polymers show resonance splitting of the bands associated with interaction between analogous groups located along the polymer chain. Thus polymers having a helical chain structure, for example, show splitting of certain vibrations into two components polarised respectively parallel to the axis of the helix and perpendicular to the plane of the helix[9], and in this case the magnitude of the splitting depends on the type of interaction between the groups involved in the vibrations. In several cases new bands are found—"amorphous" absorption bands—on passing from the crystalline to the amorphous polymer. The appearance of these absorption bands may be caused either by breakdown in the selection rules operating in the crystal or by the existence in the amorphous phase of rotational isomers which are absent in the crystalline phase. The intensity of the "amorphous" bands is usually low. This is probably

linked with a minute fraction of new isomers appearing when the substance passes between the amorphous and the crystalline states. It must be noted that the theoretical calculation of "crystalline" and "amorphous" frequencies is difficult for several reasons, and in most cases such absorption bands have been discovered experimentally in the polymers. The detection of "crystalline" and "amorphous" absorption bands and their variation with the state of aggregation of the substance are not only of theoretical interest but also of great practical value. Examination of these two types of absorption bands enables the degree of crystallinity of the polymer to be determined, as well as the melting point of the crystals, their degree of orientation, and transitions of one crystalline modification into another. In several cases their study enables conclusions to be drawn on the configuration of the molecular chains in the various states of aggregation of the polymer. The present review presents data on the development, in the infrared spectrum of several polymers, of absorption bands due to intermolecular and intramolecular interaction between the polymer chains, and on the possibility of using these absorption bands to determine physical characteristics of the polymers.

POLY(VINYL ALCOHOL) $[-CH_2-CH(OH)-]_n$

A large number of papers have recently been published, especially by Japanese workers, on investigations of the structure of poly(vinyl alcohol) (p.v.a.). It has been shown[10-13] that the conditions of polymerisation influence the stereospecificity of the resulting polymer. X-Ray results indicate that poly(vinyl alcohol) is a crystalline substance having a repeat distance of 2.52 ± 0.02 Å in the direction of stretching, independently of the conditions of polymerisation[11,14]. Fig. 1 reproduces the infrared absorption spectra of isotactic and syndiotactic poly(vinyl alcohol). The spectrum of the polymer contains bands at

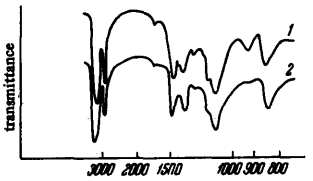


Figure 1. Infrared absorption spectrum of poly(vinyl alcohol):
1) syndiotactic (ordinary) specimen; *2*) isotactic specimen.

1141 and 916 cm^{-1} which are sensitive to intermolecular and intramolecular order. The intensity of the former band increases on heating[5] in parallel with increase in the degree of crystallinity of the polymer, determined by means of X-rays, the sorption of water, and the degree of coloration with iodine. This indicates that the absorption band at 1141 cm^{-1} is "crystalline". The intensity of the band at 916 cm^{-1} decreases[12] on such treatment (Fig. 2). As is evident from Fig. 1, this band is absent from the spectrum of isotactic specimens of the polymer. Transition from the syndiotactic to the isotactic structure is accompanied by a diminution in intensity of the absorption band at 1141 cm^{-1}.

The assignment of the absorption bands at 1141 and 916 cm^{-1} to corresponding modes of vibration is at present uncertain[15-19]. A theoretical calculation has been made[20] of the spectrum of syndiotactic and isotactic poly(vinyl alcohol), and it has been shown that the vibration $\nu(CO)A_1$ should appear in the region of 900 cm^{-1} in the spectrum of

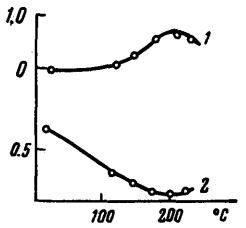


Figure 2. Effect of the temperature of heat-treatment of poly(vinyl alcohol), on relative optical densities in the bands: *1*) 1141 cm^{-1}; *2*) 916 cm^{-1}.

the syndiotactic polymer, and should be absent in that of isotactic specimens. This absorption can be identified with that at 916 cm^{-1} observed in the spectrum of syndiotactic poly(vinyl alcohol). The ratio of the optical densities in the absorption bands at 916 and 850 cm^{-1} (the latter band being taken as internal standard) has been used to determine the degree of stereoregularity of poly(vinyl alcohol) (Fig. 3) as a function of the temperature of polymerisation of the original material, which was poly(vinyl trifluoroacetate). However, it was pointed out that the ratio

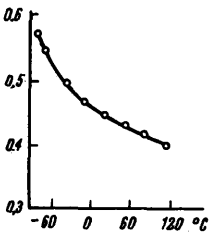
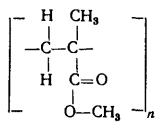


Figure 3. Dependence of ratio of optical densities of the 916/850 cm^{-1} bands on the temperature of polymerisation of poly(vinyl alcohol).

D_{916}/D_{850} itself depends on the optical density of the specimen in the region of 850 cm^{-1}. Measurements independent of the thickness of the specimen can be made when the optical density of the latter for the 850 cm^{-1} band exceeds 0.3. This fact is most probably due to the diffuseness of the reference band at 850 cm^{-1}. Estimation of the degree of syndiotacticity of a specimen from the band at 916 cm^{-1} is uncertain also because the intensity of this band (Fig. 2) depends on the degree of crystallinity of the specimen. However, the crystallinity of a specimen obtained under definite conditions of polymerisation depends on how the specimen had been prepared (humidity, temperature, etc.).

The assignment of the 1141 cm^{-1} band is uncertain. Krimm[18] originally attributed it to a ν(C–O–C) vibration, relating this absorption to the cross-linking of poly(vinyl alcohol) on heat-treatment of the polymer. Subsequently[21] this band was assigned to the vibration ν(CO) of some of the chains having intramolecular hydrogen bonds on one side of the plane of the zigzag of the main chain. It has been shown[11], however, that the isotactic poly(vinyl alcohol) model—rather than the atactic or the syndiotactic polymer—is associated with the formation of intramolecular hydrogen bonds. The 1141 cm^{-1} absorption band has been attributed[11,22] to skeletal vibrations of the atactic or syndiotactic part of the polymer. Irrespective of its assignment, this absorption band can be used to determine the degree of crystallinity of an atactic or a syndiotactic specimen of poly(vinyl alcohol).

POLY(METHYL METHACRYLATE)



Under certain conditions the polymerisation of methyl methacrylate may yield isotactic or syndiotactic poly(methyl methacrylate) or else a mixture of these forms[23–28]. Specimens of the stereoregular polymer can be crystallised, and differ from one another in glass point, melting point of the crystals, and density. X-Ray investigation of isotactic poly(methyl methacrylate) has shown[29,30] that the crystalline conformation of its chains corresponds to a 5_2 or 5_1 helix. The same conformations have been calculated theoretically[31] for the isotactic polymer. Such definite results do not exist for the syndiotactic structure: X-ray photographs of the syndiotactic polymer[29] are identical with those of an isotactic specimen. It has therefore been concluded[29] that the chains of syndiotactic poly(methyl methacrylate) also give a helical conformation. Calculations show[31] that the minimum potential energy for the syndiotactic polymer corresponds to a conformation which is closely similar to a proposed structure[32] or to a *trans*-chain. The infrared absorption spectra of these polymers differ. It has been found[33] that in the amorphous state the syndiotactic polymer is characterised by absorption bands at 1482, 1060, 910, and 822 cm^{-1}, which are very weak in an isotactic sample (Fig. 4). A method has therefore been proposed for the quantitative determination of the percentage syndiotacticity of specimens[33] from the 1060 cm^{-1} absorption band. An empirical method has been suggested[34] for calculating the stereoregularity of poly(methyl methacrylate) from the factor A, where A is a number indicating the character and degree of regularity:

$$A = 179\,(D_{1060})/D_{990} + 27;$$

$$A = 81.4\,(D_{1482})/D_{1390} - 43.$$

The parameter A has the approximate values 100–115 and 25–35 for the completely isotactic and the completely syndiotactic polymer respectively.

Hagai[35] noted an absorption band in the region of 750 cm^{-1} in the infrared spectrum, which had a rather higher frequency for isotactic than for syndiotactic poly(methyl methacrylate), and could be used in principle for quantitative calculations of the degree of stereoregularity of the polymer. Bands in the range 1050–1300 cm^{-1} are also sensitive to the intramolecular order[36]. The infrared spectra of both forms have been studied[37,38] after treatment of the specimens with heptan-4-one, which should result in their crystallisation[24]. On such treatment the infrared absorption spectrum showed the appearance of new bands in the range 1500–1600 cm^{-1}, which varied with the temperature in parallel with the X-ray pattern. It has been shown[39], however, that the appearance of these absorption bands may be due to the presence of an impurity in the specimen. The X-ray pattern observed when poly(methyl methacrylate) is treated with heptan-4-one also may be linked with the presence of this impurity. It is interesting that crystallisation of an isotactic specimen of the polymer has also been observed[34] when it was suspended in water, but no qualitative change in the spectrum was observed.

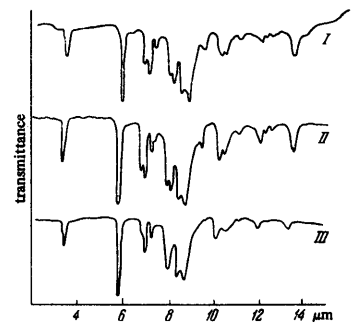
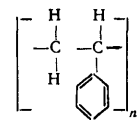


Figure 4. Infrared absorption spectrum of poly(methyl methacrylate):
I) syndiotactic; *II*) atactic; *III*) isotactic.

It is evident from the above discussion that, although differences in the stereospecificity of poly(methyl methacrylate) specimens are revealed in the infrared absorption spectrum, the quantitative determination of syndiotactic and isotactic sequences in samples is relative in character. Such determination is less accurate than the nuclear magnetic resonance (n.m.r.) method[40].

POLYSTYRENE



It has been shown[41–46] that the infrared absorption spectrum of atactic polystyrene differs from that of the isotactic polymer in both crystalline and amorphous states. Fig. 5 reproduces the infrared spectra of atactic polystyrene and the spectra of isotactic polystyrene in the melt, in carbon disulphide solution, and in the quenched and crystalline states. Three classes of changes in the infrared spectrum can be distinguished[46] on passing from an atactic to an isotactic specimen of polystyrene.

1. The intensity of several absorption bands increases, or new bands appear, in the spectrum of an isotactic specimen of polystyrene. The bands at 1365, 1297, 1260, and

1187 cm^{-1} can be regarded as of this type. Study of deuteriated derivatives of isotactic polystyrene has shown that these bands are not associated with vibration of the benzene ring.

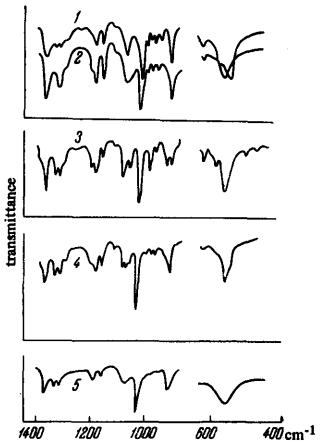


Figure 5. Infrared spectrum of polystyrene in various states of aggregation:
1) atactic; *2*) amorphous isotactic at 20°C; *3*) crystalline isotactic; *4*) isotactic dissolved in CS_2; *5*) molten isotactic.

The bands at 1365 and 1297 cm^{-1} represent deformation vibrations of CH_2 and CH groups, and the bands at 1187 and 1260 cm^{-1} stretching vibrations of the carbon chain. The appearance of absorption bands at 1187 and 1260 cm^{-1} in the spectrum of isotactic polystyrene can be explained by the formation of a helical conformation, which is characteristic of an isotactic sample[47,48]. The change in intensity of the bands at 1365 and 1297 cm^{-1}, however, is linked with some change in mode of the normal vibrations (in the present case deformation vibrations of CH and CH_2 groups) on helication of the carbon chain or on change in the spatial environment, in particular change in the interaction with other modes of vibration.

2. The band at 1070 cm^{-1} and probably that at 1312 cm^{-1} can be included in the second group of absorption bands.

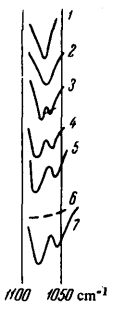


Figure 6. Absorption of polystyrene in the region of 1000 cm^{-1}: *1*) atactic; *2*) molten isotactic; *3*) quenched isotactic; *4*) isotactic dissolved in CS_2; *5*) crystalline isotactic; *6*) isotactic oriented along electric vector $E_\perp$; *7*) isotactic oriented along electric vector $E_\parallel$.

On passing from an atactic to an isotactic specimen these bands are split into two components. This splitting remains in a quenched specimen and in solution, although it is smaller (Fig. 6).

In an oriented specimen in polarised radiation the two components of the resolved bands have the same σ-dichroism. Study of deuteriated specimens has shown that these absorption bands may be due to vibrations of the benzene ring. Since both components of the resolved absorption bands exhibit σ-dichroism, it is difficult to link the splitting with intermolecular or intramolecular ordering of the chains in an isotactic specimen. The reason for splitting of this type is obscure.

3. The bands at 982, 906, 757, and 700 cm^{-1} can be placed in this group. On passing from an atactic to an isotactic specimen they are split into two components close together, which differ in polarisation. Since splitting of the bands is observed only in the crystalline state, it may be regarded as associated with the development of intermolecular order in a crystalline isotactic specimen of polystyrene. Study of deuteriated specimens shows that these absorption bands are due to vibration of the benzene ring.

The absorption range 600–500 cm^{-1} is also of interest in the spectrum of polystyrene. In the crystalline isotactic polymer absorption bands are observed at 567 and 570 cm^{-1} in this range. In solution bands are found at 560 and 544 cm^{-1}, and in the quenched state a broad band occurs at 546 cm^{-1}. The spectrum of atactic polystyrene also contains an absorption band at 546 cm^{-1} and a shoulder at 560 cm^{-1}. Takeda et al.[45] proposed using the ratio of optical densities in the bands at 546 and 560 cm^{-1} to determine the relative degree of "isotacticity" of polystyrene specimens. Pokrovskii and Fedorova[49] have recently suggested a quantitative method for calculating the degree of isotacticity from the ratio of the optical densities in these bands based on the fact that the integral intensity in the range 500–600 cm^{-1} is always constant in a solution of any specimen of polystyrene (isotactic or atactic). Most authors assign these absorption bands to $\nu_4(B_2)$ deformation vibrations of the benzene ring. Variation in the band envelope with the type of stereoregularity of a polystyrene specimen is due to the sensitivity of this vibration to various types of intramolecular order over short sections of the carbon chain. Hence we cannot agree that the integral ratio of the optical densities of the bands[49] 543/560 cm^{-1} does actually determine the absolute degree of stereoregularity in a sample. This is also indicated by the dependence of the envelope of these bands on the state of aggregation of the specimen. Unfortunately, the n.m.r. method, use of which might have given a reference point for subsequent quantitative measurement, by means of the infrared absorption spectra, of the degree of stereoregularity in polystyrene, has not at present been developed for measuring this parameter[50]. The bands at 1260, 1187, or 567 cm^{-1} can be used to determine the relative degree of crystallinity of polystyrene. Takeda[45] proposed the absorption band at 1030 cm^{-1} as internal standard for such measurements.

POLY(VINYL CHLORIDE) $[-CH_2-CHCl-]_n$

The relation between the structure of poly(vinyl chloride) [p.v.c.] and its infrared absorption spectrum over the range 400–1600 cm^{-1} has been investigated by several workers[51-58]. Attention has been directed mainly at the range 400–700 cm^{-1}, in which stretching vibrations of the

C–Cl bonds appear. Fig. 7 reproduces the infrared absorption spectrum of a feebly crystalline specimen of poly (vinyl chloride). The spectrum consists of strongly overlapping absorption bands at 693, 685, 638, and 615 cm^{-1}.

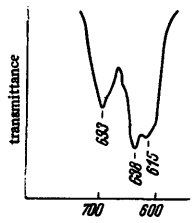


Figure 7. Infrared spectrum of poly(vinyl chloride) in the region of 600 cm^{-1}.

When such a specimen is heat-treated, and also on the polymerisation of poly(vinyl chloride) at −78°C or on channel complexes with urea, the bands at 638 and 683 cm^{-1} diminish in intensity, while fairly sharp bands appear at 603 and 640 cm^{-1} (Fig. 8). These bands disappear when

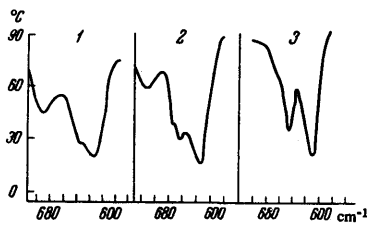


Figure 8. Infrared spectrum of poly(vinyl chloride) obtained under various conditions of polymerisation: *1*) at 50°C; *2*) at -70°C; *3*) on complexes with urea.

the polymer melts or dissolves[58]. Hence most authors[53,54] attribute the bands at 603 and 640 cm^{-1} to intermolecular interaction in the crystalline portion of the polymer. On the assumption that the low-temperature polymerisation of poly(vinyl chloride), like polymerisation on channel complexes with urea, promotes formation of a syndiotactic structure[53,55,59], the 603 and 640 cm^{-1} vibrations are assigned respectively to the B_1 and A_1 types of C–Cl-stretching vibrations. It has been shown[60,61] that the absorption band at 640 cm^{-1} has perpendicular dichroism, while the 603 cm^{-1} band has parallel dichroism, on stretching 2–2½ times; when, however, the specimen is stretched ~ 7 times, the dichroism of the 603 cm^{-1} band becomes perpendicular (Fig. 9). These effects are interpreted as reflecting a change in the intramolecular packing in the crystalline portion of the polymer at different degrees of extension.

Assignment of the absorption bands at 615, 638, 685, and 693 cm^{-1} is difficult; these bands overlap strongly, the degree of overlap depending on their relative intensities. These intensities have been shown to vary appreciably with the conditions of polymerisation of the poly(vinyl chloride) specimens, the heat-treatment of the specimens, their orientation, and finally the way in which the specimen is prepared for exposure (as tablets with potassium bromide, films, etc.). Interpretation of these absorption bands is made difficult also by the fact that no reliable data are yet available on the stereoregularity of specimens obtained under different conditions of polymerisation. X-Ray results[62] indicate that no perfect syndiotactic structure is present even in specimens of the polymer prepared by low-temperature polymerisation. Data on the structure of poly(vinyl chloride) obtained by the n.m.r. method are also as yet fairly indefinite[63,64].

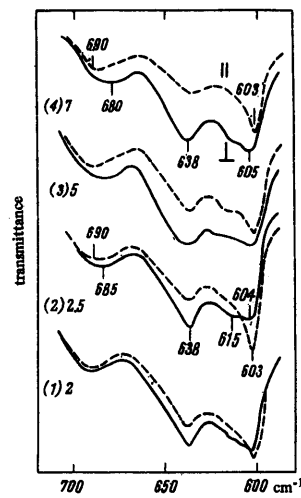


Figure 9. Dependence of dichroism in bands at 603 and 640 cm^{-1} on the stretching of isotactic poly(vinyl chloride).

Owing to the closeness of the absorption frequencies and also the uncertainty in the type of stereoregularity in the specimens, theoretical calculations on the assignment of these frequencies are also in considerable measure approximate[65]. A detailed study of secondary alkyl chlorides[57] has shown that the position of the ν(C–Cl) stretching frequencies is strongly dependent on the nature of the substituent attached to both adjacent C–C bonds located in the *trans*-position relative to the chlorine atom. In view of this, and also the dependence of the ν(C–Cl) vibration frequency on the conformation of the molecular chain, the bands at 615 and 693 cm^{-1} have been assigned to stable and unstable rotational isomers of the syndiotactic part of the polymer, while the absorption bands at 638 and 683 cm^{-1} are correspondingly assigned to unstable and stable isomers in the isotactic part of the poly(vinyl chloride) specimen. On the basis of this assignment of the absorption bands it is possible in principle to calculate several molecular parameters of the polymer: the intensity ratio of the absorption bands 615/638 cm^{-1} provides a measure of the isotactic and syndiotactic configurations present in the stable conformation; the band intensity ratios 615/693 cm^{-1} and 683/638 cm^{-1} define respectively the ratios of stable to unstable conformations in the syndiotactic and isotactic parts of the polymer. However, great caution must be exercised with respect to such measurements. Firstly, owing to the difficulties mentioned above, the assignment

of the absorption bands required for such measurements is not entirely unambiguous. Thus, for example, it is not clear why the absorption bands corresponding to the unstable rotational isomer diminish in intensity when a specimen of the polymer is heated to 180°C, whereas the quantity of unstable rotational isomers usually increases under these conditions. On the other hand, quantitative measurements are inaccurate because of the strong overlapping of the absorption bands. Somewhat better results can be obtained by examining the intensities of these bands in solutions of poly(vinyl chloride).

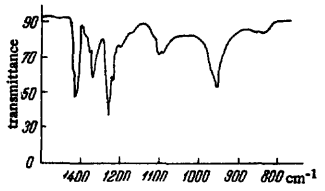


Figure 10. Infrared spectrum of poly(vinyl chloride).

The infrared spectrum of poly(vinyl chloride) in the range 1600–800 cm^{-1} is illustrated[58] in Fig. 10. The variation in absorption coefficients of a series of bands was investigated as a function of the density of the specimen, i.e. its crystallinity. The density of the specimens examined varied from 1.3887 to 1.4022. The ratio of the intensities of the bands at 1428, 1254, 1226, and 963 cm^{-1} to that of the 2920 cm^{-1} band increased linearly with the degree of crystallinity of the sample. A less marked increase occurred in this ratio for the bands at 1434, 1355, and 831 cm^{-1}. At the present time the assignment of these bands by different authors[58,66] is ambiguous. Irrespective of the assignment, these bands are sensitive to the three-dimensional order in the polymer. It is noteworthy that the sign of the dichroism of the 963 and 1254 cm^{-1} bands depends on the degree of stretch of the specimen (just as with the 603 cm^{-1} band).

POLY(VINYLIDENE FLUORIDE) $[-CH_2-CF_2-]_n$

A study has been made[67] of the infrared spectra of poly(vinylidene fluoride) in crystalline and amorphous states. The spectrum of films of this polymer prepared from solution in dimethyl sulphoxide is found to contain absorption bands at 1075, 980, 855, 798, and 762 cm^{-1}. These bands diminish in intensity or disappear when the specimens are heated above 165°C, which corresponds to the melting point of the polymer. Cooling the specimen to room temperature results in the reappearance of these absorption bands. Analogous behaviour is shown by the weak bands in the region of 3700, 3620, and 3380 cm^{-1}. All the above bands can be regarded as "crystalline", since they characterise the intermolecular ordering of the polymer chains. The 740 cm^{-1} band can be regarded as "amorphous", since its intensity increases when the specimen melts.

The infrared spectrum of poly(vinylidene fluoride) has been investigated[68] in greater detail in the range 3000–400 cm^{-1}. In this case films of the polymer were prepared from a solution in boiling acetone. The spectrum of such specimens contains bands at 484, 510, 840, 1073, 1180, and 1235 cm^{-1}, which disappear when the polymer is heated to 220°C. Nor are these bands observed in a spectrum of a solution of the polymer in acetone. For all these reasons the bands can be regarded as "crystalline". The crystalline modification of poly(vinylidene fluoride), whose spectrum is characterised by the above six bands and by a definite X-ray pattern, has been called the α-form. The bands at 600, 740, and 905 cm^{-1}, the intensity of which increases when the polymer melts, are regarded as "amorphous". The content of the amorphous phase in the polymer, determined by means of these bands, is ~ 50%. When a film of the polymer which has been heated to 220°C is cooled to room temperature, new sharp bands appear in the spectrum at 488, 531, 612, 765, 796, 857, 977, 1071, 1152, 1185, 1215, and 1385 cm^{-1}, which are characteristic of the crystalline state of the polymer. The variation in these bands with temperature, together with X-ray investigations, suggest that in this case another crystalline modification of the polymer—the β-form—can exist. Study of the spectra of oriented specimens of poly(vinylidene fluoride) in polarised infrared radiation confirms the existence of α- and β-forms[69]. The different crystalline forms correspond to different conformations of the polymer chain.

Analysis of data obtained from the infrared absorption spectra, together with X-ray structural analysis, shows[70–72] that in the α-conformation the molecular chains have a planar zigzag structure, and in the β-modification they have the TG–TG′ conformation. The existence of a third conformation has been suggested[72], the infrared spectra of which differ from that of the α-conformation in the intensities of certain absorption bands. The most marked differences are observed in the range 250–400 cm^{-1}.

POLYAMIDES

Many authors have been concerned in correlating[73–78] the infrared spectra of polyamides with the intermolecular and intramolecular order in the polymer. It has now been firmly established[79–83] that, depending on the number of methylene groups between the amide groups or on the treatment of the specimens, polyamides can exist in three crystalline modifications—α, β, and γ—or contain these forms together in various proportions. Whereas the α- and β-forms have a monoclinic crystal cell, in which the methylene chain is in the form of a flat zigzag lying in the same plane as the amide group, the γ-configuration has hexagonal packing (the plane containing the amide group is inclined at ~ 30° to the plane of the methylene chain).

Fig. 11 gives the infrared spectra of polycaprolactam in α- and γ-forms and of molten and quenched specimens of the polyamide. It is seen that the monoclinic α-form is characterised by absorption bands at 575, 692, 930, 960, 1201, 1420, 1470, and 1477 cm^{-1} (I). The crystalline γ-form is represented by bands at 625 and 711 cm^{-1} (II). Bands at 976, 1170, 1440, and 1460 cm^{-1} (III) are present in the γ-modification and in the molten polyamide, but are weaker or completely absent in polymers containing only or predominantly the α-modification. The bands at 590, 700, 1240, and 1280 cm^{-1} (IV) increase in intensity on fusion of the specimens. Bands of group I are associated[75,76] with the conformation of the molecular chain in the crystal cell characteristic of the α-form; the bands forming group II are probably linked with the intermolecular order in the γ-form of the crystals; those of group III are associated with the conformation in which the methy-

lene chain is not in the same plane as the amide group; and group IV are associated with the appearance of a coiled conformation of the molecular chains on fusion of the polyamides. A good criterion of the presence of α- and γ-crystalline forms is the position of the amide band[84] V, which in the α-form is located in the range 680–690 cm^{-1}, whereas in the γ-form it lies in the range 711–730 cm^{-1} (Fig. 12).

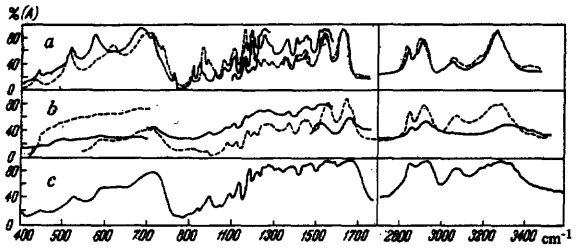


Figure 11. Infrared spectrum (A = absorption, %) of a polyamide: *a*) highly crystalline polymer ($\alpha + \beta$-form), the broken line representing the γ-form; *b*) molten polymer (245°C), the broken line representing the quenched polymer at 110°C; *c*) quenched polyamide at 20°C.

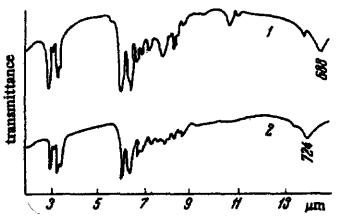


Figure 12. Position of amide V in a polyamide in the modifications:
1) α; *2*) γ.

Since a partly crystalline polyamide at ordinary temperatures exhibits bands characteristic of both α- and γ-forms of the crystal cell, the problem of determining the degree of crystallinity in polyamides is complicated. The 930 cm^{-1} band is most widely used[73,74,86] for this purpose. Such determination is valid provided that the specimen contains only or predominantly the α-form. The intensity of the band is then proportional to the degree of crystallinity of the polymer (Table 1). In all other cases measurement of the crystallinity on the basis of the 930 cm^{-1} band may result in large errors. As already mentioned above, the most convenient method is to determine the degree of crystallinity from "amorphous" absorption bands. However, such bands at 590, 700, 1240, and 1270 cm^{-1} in polyamides overlap other bands, and are unsuitable for quantitative determinations.

Novak et al.[86] have proposed a method for estimating the degree of crystallinity of poly-ϵ-caprolactam from the absorption bands at 930, 1076, and 1118 cm^{-1} (the latter two of which were regarded as "amorphous"). A complicated dependence of crystallinity on orientation was discovered: the orientation of quenched fibres increases the crystallinity, and the orientation of fibres of high crystallinity produces a decrease; finally, with degrees of crystallinity of 18–20% the content of the crystalline phase is unaffected by deformation.

Table 1. Determination of crystallinity in a polyamide as a function of the heat-treatment of the specimen.

Crystallisation temp., °C	Crystallinity, %, from 930 cm^{-1} band	Crystallinity, %, from density	Crystallisation temp., °C	Crystallinity, %, from 930 cm^{-1} band	Crystallinity, %, from density
—	23	24	132	29	25
—	24	24	132	32	22
—	25	27	160	27	20
—	24	22	160	30	41
100	29	29	160	41	41
100	30	29	180	27	25
100	30	29	180	42	43
100	30	29	180	44	44
100	29	21	185	45	43
100	25	17	185	45	53
100	22	17	185	46	51
132	35	36	210	48	50
132	35	36	210	46	57
132	36	36	210	47	57
132	36	36	210	48	56
132	28	23	210	51	55

POLYPROPYLENE

$$\left[-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}H-\right]_n$$

The spectrum of isotactic polypropylene contains several strong and moderately strong absorption bands in the range 1200–800 cm^{-1} (Fig. 13). These bands are interesting because their intensity depends greatly on the degree

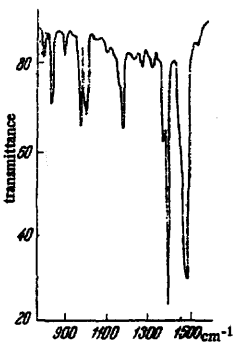


Figure 13. Infrared spectrum of crystalline isotactic polypropylene.

of microtacticity and crystallinity of the specimen, as well as on its state of aggregation. Thus the bands at 841, 997, and 1167 cm^{-1} disappear at 180°C, the melting point of polypropylene[87–90]. The bands at 841, 973, 997, 1153, and 1167 cm^{-1} are absent in specimens of polypropylene which has been prepared on non-stereospecific catalysts[91,92].

In a quenched specimen[93,94] the differential intensity of the bands at 841, 997, and 1167 cm^{-1} is diminished, while those at 973 and 1153 cm^{-1} remain practically unchanged. The 973 cm^{-1} absorption band remains, though diminished in intensity, when polypropylene is dissolved in benzene. X-Ray examination of quenched propylene shows[91] a peak at $2\theta = 22.2°$ besides an amorphous halo: i.e. the intermolecular ordering of molecular chains is partly preserved in a quenched specimen.

Differences in the infrared absorption spectra of different polypropylene fractions, specimens of different degrees of crystallinity, and specimens examined at 20° and 180°C may be associated with variation in both intramolecular and intermolecular order. The behaviour of the bands at 997, 841, and 1167 cm^{-1} on fusion and quenching of the polymer may indicate that these bands are due to the intermolecular order in polypropylene specimens. This order disappears in molten polypropylene, but is partly preserved in a quenched specimen, although X-ray examination indicates such a specimen to be amorphous. This explanation[96,97] is consistent with the fact that the intensity of the 997 cm^{-1} band increases in proportion to the degree of crystallinity of the specimen. The 1153 and 973 cm^{-1} bands may be due to intramolecular order in isotactic polypropylene[93,94]. Natta has shown that the molecular chains in isotactic polypropylene have the configuration of a 3_1 helix.

The Raman spectrum at 20° and 180°C has recently been obtained[98] for specimens of isotactic polypropylene (Fig.14). The changes produced in the Raman spectrum by fusion of the specimen are the same as observed in the infrared absorption spectrum. Since the unit cell of isotactic polypropylene belongs to the symmetry group C_{2h} and has a centre of inversion, this may be expected to lead to mutual exclusion of the frequencies in the Raman and infrared absorption spectra. As these spectra are identical at 20°C, it may be assumed that the spectrum of polypropylene is determined mainly by the chain structure alone.

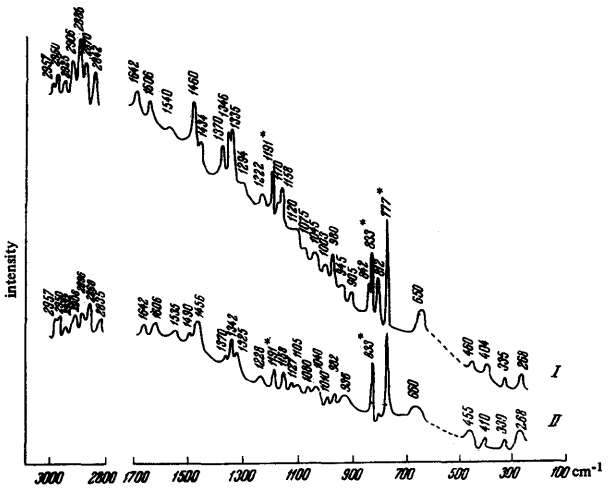


Figure 14. Raman spectrum of isotactic polypropylene: *I*) crystalline; *II*) molten.

Thus the absorption bands at 997, 841, and 1167 cm^{-1} may be associated either with intermolecular ordering of the polypropylene chains or with intramolecular order over large sections of the chains. The 974 and 1153 cm^{-1} bands, however, are probably linked with short-range intramolecular order. It thus becomes possible to measure[93,94,99] the relative "microtacticity" of polypropylene specimens from the intensity of the 974 cm^{-1} band, and the intermolecular ordering of the molecular chains from the 997 cm^{-1} band. A method has been proposed[100] for estimating the degree of isotacticity of polypropylene from the lack of symmetry of the former band. Appropriate fractions of the polymer and mechanical mixtures thereof were used to calibrate the method. The percentage isotacticity determined by this method was shown to agree well with the degree of crystallinity of the same specimen measured by means of the 997 cm^{-1} band at medium values of the isotacticity, and to differ markedly for its extreme values.

Fig. 15 shows the spectrum[101] of isotactic and atactic polypropylene in the range 410–100 cm^{-1}. It is seen from Figs. 15 and 16 that, whereas the spectrum of the isotactic polymer contains well separated absorption bands at 321, 251, 210, 200, 169, and 155 cm^{-1}, the atactic polymer has a diffuse absorption spectrum. There is no exact assignment of these bands to a definite type of vibration. In view of the sign of the dichroism, it is assumed that the bands at 398, 251, 200, and 155 cm^{-1} are due to vibrations of symmetry A, and those at 321, 210, and 169 cm^{-1} to symmetry E ($2\pi/3$) (Fig. 16). It may be supposed that these bands are due to skeletal deformation vibrations or correspond to frequencies of internal rotation in the polymer.

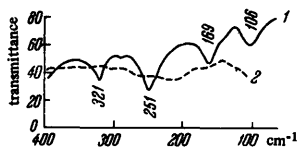


Figure 15. Infrared spectrum of polypropylene: *1*) crystalline isotactic; *2*) atactic.

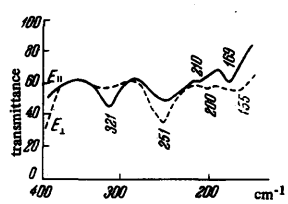


Figure 16. Infrared spectrum of isotactic polypropylene in polarised radiation.

Natta and his coworkers[102,103] synthesised syndiotactic polypropylene at low polymerisation temperatures (−70°C) on homogeneous catalytic systems obtained from a vanadium compound. The resulting polymer had fairly low crystallinity, which probably indicated that it was very inhomogeneous. The infrared spectrum of syndiotactic polypropylene differs somewhat from that of an isotactic specimen[104,105]: several absorption bands, e.g. at 997 and 458 cm^{-1}, are absent from the spectrum of syndiotactic polypropylene, and many bands are either displaced in frequency compared with the spectrum of an isotactic specimen or are characteristic only of this spectrum, e.g. 1005 and 970 cm^{-1}.

Zambelli et al.[104] suggested a method for determining the degree of syndiotacticity of polypropylene specimens using the ratio of the optical densities in the bands at 11.53, 2.32, and 2.35 μm:

$$A = D_{11.53}/^1/_2 (D_{2.32} + D_{2.35})$$

where A is the relative syndiotacticity index. It must be noted that the index is strongly dependent on temperature over the presumed melting range of the specimen[106].

A helical conformation has been suggested for syndiotactic polypropylene. However, a new crystalline modification of syndiotactic polypropylene has been obtained[107]. This modification is formed by the orientation of a quenched specimen of the syndiotactic polymer. The molecular chains then form a planar zigzag. The new modification is characterised by absorption bands at 1005, 1130, 960, and 830 cm^{-1} having parallel polarisation, and bands of lower intensity in the region of 1320 and 820 cm^{-1} having perpendicular polarisation.

The study of deuteriated specimens of polypropylene has enabled several of the above absorption bands to be related to vibrations of certain groups[87,105] (Table 2).

Table 2. Assignment of absorption bands of polypropylene.

Absorption bands, cm^{-1}		Type of vibration
syndiotactic	isotactic	
866	841	CH_2 rocking (A), CH_3 rocking (A), C–C stretching (A)
962	973	CH_3 rocking (A), CH_2 rocking (A), C–C stretching
977	997	C–C stretching (A), CH_3 rocking (A), CH_2 rocking (A)
1083	1102	C–C stretching
1005	1042	
1152	1153	CH_3 wagging
1157	1167	CH_3 wagging, C–C stretching (A)
485	458	C–C deformation

POLYETHYLENE $[-CH_2-CH_2-]_n$

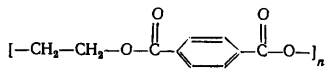
Polyethylene has a simple absorption spectrum, which has been well deciphered[108–110]. The greatest interest is presented by the absorption bands at 720, 730, 1308, 1464, and 1473 cm^{-1}, which are present in the partly crystallised polymer. In the amorphous state the band at 730 cm^{-1} has disappeared from the infrared spectrum, while that at 1303 cm^{-1} has increased in intensity; the doublet 1464–1473 cm^{-1} has been replaced by a single band at 1460 cm^{-1}.

It has been shown theoretically[109,110] that the appearance of the doublets 720–730 and 1464–1473 cm^{-1} is due to resonance interaction of deformation vibrations (rocking and wagging respectively) of methylene groups in the crystal cell, but the polarisation of the resolved components obtained in these papers did not agree with that determined experimentally.

It has since been shown that the type of splitting and the polarisation of the bands can be explained[111] by choosing an appropriate potential taking into account the interaction not only of hydrogen atoms adjacent to the chains but also of more remote hydrogen atoms. The 1303 cm^{-1} band is of especial interest, since it becomes stronger when polyethylene melts, which makes it possible to determine quantitatively the crystalline content[112–114] of the polymer by a method independent of X-ray examination. This band is assumed[112] to be characteristic of the presence of a skew rotational isomer in the amorphous part of the polymer. The presence of rotational isomers in polyethylene[115] has been confirmed also by an investigation of the stretching of the polymer. The 1460/1303 band absorption coefficient ratio increases when polyethylene is stretched by 1000% of its original length, owing to transition of the skew isomer into a *trans*-isomer. The conversion of skew isomers into *trans*-isomers on stretching has since been confirmed by measuring the energy changes accompanying stretching of cross-linked polyethylene[116].

The absorption bands at 1308, 1350, and 1365 cm^{-1} have been used[117,118] to investigate polyethylene single crystals. A method has been suggested[117] which will in principle enable us, by means of the variation in the intensities of these absorption bands, to distinguish the amount of disordered material in the polymer from the amorphous part formed when the polymer is packed into folded crystals.

POLY(ETHYLENE TEREPHTHALATE)



Spectroscopic study of this polymer[119–121] indicates that the changes observed in the spectrum (Fig. 17) on passing from the crystalline to the amorphous state are associated with rotational isomerism. Table 3 lists the absorption band frequencies which are sentitive to a change in crystalline state[119]. It has been shown that these bands do not completely disappear in the above transition.

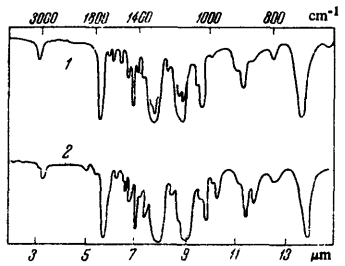


Figure 17. Infrared spectrum of poly(ethylene terephthalate):
1) amorphous; *2*) crystalline.

The absorption spectrum of a model compound (ethylene dibenzoate) in solution contained the same absorption bands as did the molten polymer. It might be supposed that the changes in intensity of the polymer bands indicated in Table 3 were due to intermolecular or intramolecular interaction. Examination of the model compound (ethylene dibenzoate) showed that the intensity remained unchanged on dissolution of the compound in carbon tetrachloride over a wide range of concentrations. In crystalline ethylene dibenzoate, on the other hand, the 1375 and 1100 cm^{-1} bands disappear: they are "frozen out". All this indicates that the bands in Table 3 are not due to intermolecular interaction, but represent different conformations[119] of the polymer.

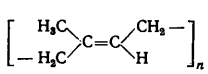
It may thus be supposed that the observed changes in the spectrum of poly(ethylene terephthalate) are associated with the phenomenon of rotational isomerism. When the polymer is stretched, a change is observed[121] in the intensities of the absorption bands in Table 3. It is interesting that the absorption bands which are most sensitive to a change in conformation of the chain are due to normal vibrations including ester and ethylene groups.

Table 3. Absorption bands sensitive to crystalline state.

ν, cm^{-1}	Change in intensity with increasing crystallinity
1475	increases
1375	decreases
1340	increases
1130	increases
1100	decreases
975	increases

An investigation has been made[122] of the dependence on the applied load of the positions of the absorption band maxima associated with vibrations of the main chain and side-chains for poly(ethylene terephthalate), polyethylene, and poly-ϵ-caprolactam. This showed that under load the absorption maxima associated with the main chain move to lower frequencies, while those associated with side-chains are shifted to higher frequencies. These results enable infrared spectroscopy to be used to study the stress in bonds in a polymer subjected to tension, and to compare the mechanical stress produced in the specimen with the true stress acting on a deformed bond.

GUTTA-PERCHA



At 20°C gutta-percha can exist in two crystalline modifications—α and β—melting at 65° and 56°C respectively. α-Gutta-percha is the stable modification, which can be obtained from a solution of the polymer; β-gutta-percha is obtained by rapidly cooling the amorphous polymer which has been heated to 70°C. X-Ray data indicate[123] that the unit cell of β-gutta-percha has the parameters—a = 7.78 Å, b = 11.78 Å, and c = 4.72 Å—and contains four isoprene groups. Data on the parameters of the unit cell of the α-form are more uncertain. α-Gutta-percha has a molecular period of c = 8.9 Å, which is produced by two isoprene groups, not one as with β-gutta-percha, where c = 4.72 Å. The two modifications are obviously rotational isomers.

The infrared spectra of the α- and β-forms of gutta-percha differ markedly in frequency and intensity in the range 1700–400 cm^{-1} (Fig. 18).[124–126] Characteristic absorption bands of α-gutta-percha are located at 1150, 1100, 1055–1035 (doublet), 865, 490, and 470 cm^{-1}. β-Gutta-percha is characterised by absorption bands at 1290–1270 (doublet), 1160, 1108, 760, 603, and 475 cm^{-1}. Table 4 gives the probable assignment of these bands. Comparison of the spectrum of crystalline gutta-percha with the infrared absorption spectrum of a melt of α- and β-forms shows that the bands at 1215, 890, 865, 805, 615, 490, and 470 cm^{-1} are "crystalline" in the spectrum of the α-modification. The absorption bands at 1220, 882, 800, 760, 603, and 475 and the 1290–1270 cm^{-1} doublet are "crystalline" in the spectrum of β-gutta-percha. The difference in the frequencies of the "crystalline" bands due to α- and β-gutta-percha is associated with the difference in structure between their unit cells, which are made up of chains having different configurations. These vibrations most probably arise as a result of intermolecular resonance interaction of corresponding vibrations. This certainly applies to the doublets 1055–1035 and 1290–1270 cm^{-1} in the absorption spectra of α- and β-gutta-percha respectively. With polarised radiation the absorption bands of these doublets show opposite polarisation, and in a melt the doublets are replaced by absorption bands at 1040 and 1260 cm^{-1} respectively.

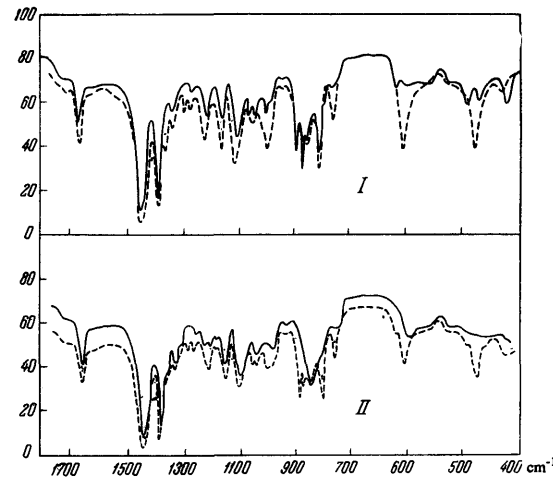


Figure 18. Infrared spectrum of gutta-percha: *I*) α-gutta-percha (full curve) and β-gutta-percha (broken curve); *II*) molten gutta-percha (full curve) and $\alpha + \beta$-gutta-percha (broken curve).

Table 4. Assignment of "crystalline" absorption bands (ν, cm^{-1}) in gutta-percha.

Modification		Assignment
α	β	
	1290	$\gamma_w(CH_2)$, $\gamma_t(CH_2)$
	1270	
1215	1220	
1150	1160	ν (C—C), $\gamma_r(CH_2)$
1100	1108	
1055		
1035		
890	882	
865	760	$\gamma_r(CH_2)$
805	800	
490	603	C—CH_3, C—C—C
475	475	C—C=C deformation
420	425	

In the range 400–700 cm^{-1} the absorption in molten α- and β-gutta-percha and its solution in carbon disulphide is diffuse in character[126]. The appearance of distinct, sharp

absorption bands in this range on crystallisation of the polymer either in α- or β-form, is linked with a change in the selection rules accompanying the transition from amorphous to crystalline gutta-percha. Independently of the reason for the appearance of "crystalline" bands in the α- and β-forms, it is fundamental that these bands characterise, directly or indirectly, the conformation of the chains in the differing crystal cells of α- and β-gutta-percha. This provides a method for studying the crystallinity of the two forms, their melting points, etc. It is also very important that the presence of bands characteristic of α- and β-forms has enabled the rotational-isomerism mechanism of the stretching of polymers to be proved unambiguously[115,126,127]. It has been shown that, when the α-crystalline form of gutta-percha is stretched, it passes into the β-form. This corresponds to conversion of an isomer of shorter chain length (the α-form) into an isomer of longer chain length (the β-form).

The infrared spectra of the α- and β-modifications of gutta-percha differ not only in their "crystalline" bands. The 1108 cm^{-1} band in α-gutta-percha and the 1100 cm^{-1} band in β-gutta-percha are of interest. They are probably due to ν(C–C) vibrations. The 1100 cm^{-1} band characterises the α-conformation of the chain, while the closely situated 1108 cm^{-1} characterises the β-conformation. Fig. 19 shows the infrared spectra in the range 1000–1100 cm^{-1} for the two modifications dissolved in carbon disulphide and for molten gutta-percha. In the spectrum of crystalline α-gutta-percha the main band at 1100 cm^{-1} is accompanied by a weak band at 1108 cm^{-1}, which indicates that the polymer contains, besides chains in the α-conformation, sections of molecular chains in the β-conformation.

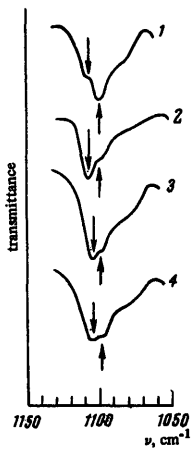
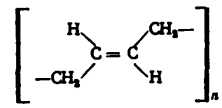


Figure 19. Infrared spectrum of:
1) α-gutta-percha at 20°C; *2*) β-gutta-percha at 20°C; *3*) gutta-percha dissolved in CS_2; *4*) molten gutta-percha at 70°C.

The spectrum of crystalline β-gutta-percha contains a weak band due to the α-conformation. Two absorption bands, corresponding to the α- and β-conformations of the chain, can also be distinguished in the spectrum of a solution in carbon disulphide and of the melt. The presence in the spectrum of gutta-percha of bands characteristic of both conformations provides a method for determining their contents[126] in crystalline specimens at 20°C. It has been found that crystalline α-gutta-percha contains 60% of chains in the α-conformation and 40% in the β-conformation. Crystalline β-gutta-percha contains 60% of chains in the β-conformation and 40% in the α-conformation.

POLY-*trans*-1,4-BUTADIENE



This polymer can exist in two crystalline modifications[128–130]. Modification I exists up to ~ 50°C. Over the temperature range 50–70°C two modifications are present together. Above 70°C the polymer exists as modification II, which gradually melts with rise in temperature, and at 130°C the polymer is in the amorphous state. The infrared spectrum of this polymer (Fig. 20) is characterised by

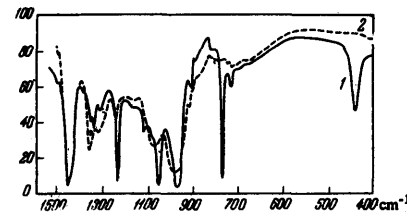


Figure 20. Infrared spectrum of poly-*trans*-1,4-butadiene:
1) crystalline; *2*) amorphous.

"crystalline" absorption bands at 445, 772, 1121, 1235, and 1051 cm^{-1}, the intensity of which decreases with rise in temperature, and "amorphous" bands at 1350 and 1308 cm^{-1}, whose intensity increases with rise in temperature[128]. Fig. 21 shows that the temperature dependence of optical density in "crystalline" and "amorphous" bands[130] is in opposite senses, being associated with transition of modification I into modification II and their fusion. This result is consistent with X-ray investigations[130].

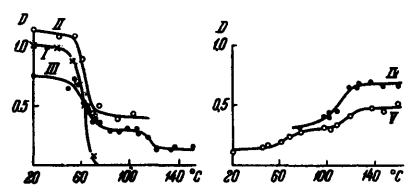


Figure 21. Temperature variation of optical density of poly-*trans*-1,4-butadiene in "crystalline" bands (cm^{-1}):
I) 770; *II*) 1051; *III*) 1235; and in "amorphous" bands at:
IV) 1308; *V*) 1353.

The "crystalline" absorption bands of poly-*trans*-1,4-butadiene can be divided into two groups. The bands at 445, 770, and 1121 cm^{-1} disappear completely on fusion of

the polymer, and their appearance on crystallisation is probably associated with a change in the selection rules. The bands at 1235 and 1051 cm^{-1} become much stronger on crystallisation, but do not disappear completely in the melt. They may be associated with the retention in the melt of a rotational isomer characteristic of the crystalline state of the polymer. The absorption bands at 1308 and 1353 cm^{-1} are especially interesting. Bands at 1353 and 1303 cm^{-1} in polyethylene were assigned to the vibration $\gamma_w(CH_2)$ in the amorphous portion of the polymer[18,113]. In poly-*trans*-1,4-butadiene they can probably be assigned to this type of vibration. These absorption bands have been used for the quantitative determination of the crystalline portion in an unoriented specimen.

The process of orientation of poly-*trans*-1,4-butadiene has been investigated in work[131] on the variation in the intensity and dichroism of the bands at 1308, 1235, 1051, 772, and 445 cm^{-1}. This has shown that the quantity of crystalline material in the polymer increases in the course of orientation, and at degrees of orientation of ~ 45% the crystalline portion is completely oriented along the axis of stretch. Calculation of the angle of orientation between the direction of the dipole moment and the axis of the molecule for the vibration $\delta(CH_2)$ showed that the molecular chains in the crystalline portion of modification I of poly-*trans*-1,4-butadiene do not have a planar *trans*-conformation but are somewhat twisted.

In conclusion we give a published[131] assignment of the "crystalline" and "amorphous" bands in this polymer (Table 5).

Table 5. Assignment of "crystalline" and "amorphous" bands in the spectrum of poly-*trans*-1,4-butadiene.

At 20°C, "crystalline"					At 150°C, "amorphous"	
ν, cm^{-1}	intensity	$R = D_{\parallel}/D_{\perp}$	α, deg	assignment	ν, cm^{-1}	intensity
1350	m.	?	—	(CH_2) amorphous	1354	m.
1340	m.	?	—	(CH_2) crystalline	—	–
1308	w.	?	—	(CH_2) amorphous	1313	m
1235*	s.	10.72	0—23	(CH_2) crystalline	1243	w.
1121	w.	?	—	crystalline	—	–
1051*	s.	3.53	31—37	crystalline	1063	m.
772*	s.	?	—	(CH_2) crystalline	—	–
445*	s.	0.65	62—61	crystalline	—	–

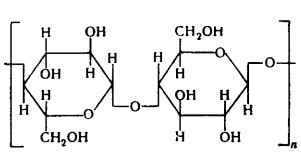
* Band frequencies differ by 2 cm^{-1} with $E_{\parallel}$ *and* $E_{\perp}$.

Intensity: m. = medium; w. = weak; s. = strong.

A question mark (?) indicates that the sign of the polarisation is difficult to determine.

The symbol α denotes the angle between the direction of the dipole moment and the direction of orientation.

CELLULOSE



The view is widely held, based on the results of physical methods of investigation, that the supermolecular structure of cellulose contains highly ordered (crystalline) and less ordered (amorphous) chain segments. Several workers do not accept the presence of strict three-dimensional ordering of chains in this polymer[132]. A more detailed discussion of this matter will be found in a monograph[133].

X-Ray examination shows that cellulose can exist in various crystalline modifications (I–IV). The arrangement of the atoms in the unit cells has not been established definitely, and significant information can therefore be obtained from a study of the disposal of atomic groupings by means of polarised infrared radiation.

The early spectroscopic investigations of cellulose showed that hydroxy-groups in it were hydrogen-bonded[134,135]. This conclusion was based on an examination of the first overtone of the hydroxyl vibration. The nitration of cellulose was shown[135] to be accompanied by the release of hydroxyls from hydrogen-bonding. The shift in the band 2ν(OH) to higher frequencies in the spectrum of cellulose II than in that of cellulose I was explained by the weakening of hydrogen bonds in the former modification. A recent spectroscopic investigation of specimens of methylcellulose of low degrees of substitution indicates that increase in the degree of methylation is accompanied by a diminution in the number of hydroxyls involved in the stronger hydrogen bonds[136].

X-Ray data indicate the existence of various types of hydrogen bonds in the crystallographic unit cell of cellulose. This can be established by examining the hydroxyl bands in the infrared spectra.

The OH band, characteristic of a hydrogen bond, has five peaks[137] in the spectrum of highly crystalline cellulose I (*Valonia ventricosa*). Interesting results have been obtained by investigating deuteriated samples of celluloses. The method of deuterium exchange enables the absorption of associated OH groups, present only in the crystalline portion of a polymer, to be observed, since in the early stages deuteriation does not affect the crystals. It has been established[138] by this method that the crystalline portion of cellulose II exhibits four OH peaks, at 3484, 3444, 3322, and 3163 cm^{-1}, characteristic of a hydrogen bond (Fig. 22). The OH absorption bands in crystalline model compounds—cellotetraose and cellopentose—have been observed at the same frequencies. On deuteriation the frequency of the OH peaks in cellulose II is found[136] to decrease by the same amount. All this suggests that various types of hydrogen bonds are present in the crystalline portion of cellulose II. It must be stressed, however, that great caution must be exercised in establishing a relation between the number of peaks of OH- and NH-stretching vibrations and the number of types of hydrogen bonds, since individual peaks may be caused by other factors[138–140].

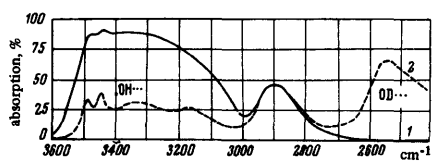


Figure 22. Viscose rayon film:
1) before deuteriation; *2*) after deuteriation for 4 h.

It has been definitely established[140,141] that all hydroxy-groups in the crystalline segments of celluloses I–IV are hydrogen-bonded, since no OH band characteristic of unbonded hydroxyl has been observed in the spectrum.

Replacement of OH by OD in the amorphous portion of cellulose specimens has permitted a detailed investigation of the form of the OH absorption band in the crystalline portion of celluloses I–IV. All four modifications of cellulose were shown[142] to have different spectra (in the range 3100–3600 cm^{-1}). Other workers have concluded[143], however, that all the crystalline forms can be represented by only two types of spectra (in the range 400–3700 cm^{-1}). The difference in the spectra is explained by rotational isomerism of the hydroxymethyl group[143], it being assumed (contrary to Ref. 144) that only two rotational isomers are present in cellulose.

Interesting results have been obtained from a study of oriented deuteriated cellulose specimens in polarised infrared radiation[145,146]. Figs. 23 and 24 show the OH and OD bands observed under these conditions. It is seen that the parallel component is more intense than the perpendicular component. This suggests that in cellulose crystals a large number of OH bonds are arranged parallel—not along the normal—to the chain direction. The hypothesis has been put forward that some of the hydroxyls form part of an intramolecular hydrogen bond between $O_{(3)}$ of one unit and $O_{(6)}$ of another, and between $O_{(5)}$ and $O_{(6)}$, which also belong to different units[146]. The presence in cellulose of intramolecular together with intermolecular hydrogen bonds has been pointed out also by other workers[147].

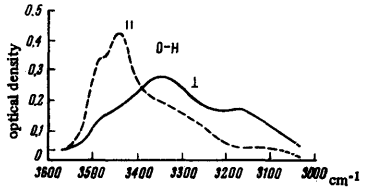


Figure 23. Dichroism of crystalline segments of cellulose II in the region of OH vibrations.

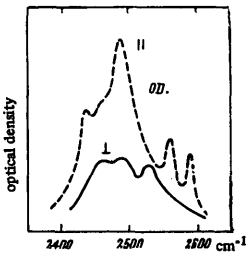


Figure 24. Dichroism of crystalline segments in region of OD vibrations.

The intensities of the bands at 900 and 1430 cm^{-1} are sensitive to structural changes in cellulose[149–151]. Thus they depend on the degree of crystallinity of the specimens[149]. When a sample was ground into powder, the intensity of the latter band diminished, and at the same time that of the 900 cm^{-1} band increased. Hence the 1430 cm^{-1} band was regarded as "crystalline", and the 900 cm^{-1} band as "amorphous". The degree of crystallinity of cellulosic materials is determined from the intensity ratio of the bands at 1430 and 900 cm^{-1}. Other workers have found that these bands change in intensity on passing from cellulose I to cellulose II (on mercerisation), and on this basis have proposed a spectroscopic method for determining this transition[150]. It has been noted also[151] that the intensities of these bands change both with the degree of crystallinity of the specimen and with the extent of conversion of cellulose I into cellulose II. These results show that further study is required of the use of these bands to determine the degree of crystallinity of cellulose and to assess the process of mercerisation. Mention must be made here of work[152] showing that the 900 cm^{-1} band in various specimens of cellulose is composite, consisting of at least two components (Fig. 25). Differences in the position and the intensity of the components in the region of 900 cm^{-1} in different samples of cellulose may be associated with rotational isomerism. A band at 560 cm^{-1} is also sensitive[143] to the transition I → II.

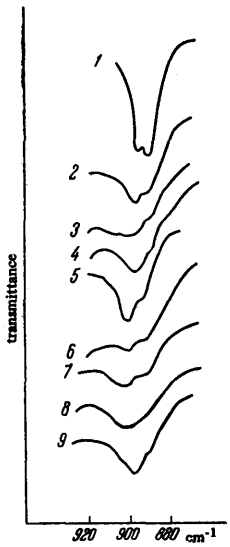


Figure 25. Spectra of:
1) crystalline cellobiose; *2*) amorphous cellobiose; *3*) natural cotton; *4*) mercerised cotton; *5*) cotton which has been activated with ethylenediamine; and of sulphite wood celluloses intended for chemical processing:
6) American; *7*) Japanese; *8*) Priozerskii Kombinat; *9*) as (*8*) mercerised.

The method of infrared spectroscopy is used to estimate the crystallinity of cellulose and assess the conversion of cellulose I into cellulose II. As already mentioned, deuterium exchange takes place in the amorphous portion of cellulose, leaving the crystalline portion practically unaffected. This enables the contents of crystalline and amorphous materials in cellulose to be estimated from the relative intensities of the OH and OD bands[148].

The intensity ratio of bands at 1372 and 2900 cm^{-1} has recently been proposed[153] for estimating the crystallinity of celluloses I and II. The former is regarded as the crystallinity band, while that at 2900 cm^{-1} is used as internal standard. This intensity ratio correlates with the crystallinity of the polymer determined from X-ray data, density, and the sorption of moisture. This correlation is

stated to be of the same form for celluloses I and II as for cellulose which has been treated with alkali, which is not the case with the intensity ratio of the bands at 1430 and 900 cm^{-1}.

It must be pointed out that a_{1372}/a_{2900} does not correlate sufficiently well with the crystallinity of cellulose determined by other physical methods[153]. The overlapping of the absorption band at 1372 cm^{-1} with adjacent bands, and also the difficulty of allowing for the background, are the reasons why structural changes in cellulose cannot be assessed with sufficient accuracy from this ratio.

A method has been proposed[154] for measuring the extent of mercerisation of cellulose from the ratio of the optical densities in infrared bands at 1375 and 1325 cm^{-1}. The sensitivity of this ratio to mercerisation has been established by comparing spectroscopic with X-ray data.

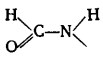
The present review has reported work on the structure of cellulose. Information on the spectroscopic investigation of cellulosic materials (the oxidation of cellulose, its ethers, and its esters, the study of substituted celluloses, etc.) can be found in several publications[155-157].

POLYPEPTIDES

The primary reason for interest in this class of polymers is that polypeptides represent one of the closest analogues of proteins. As a consequence, the application of infrared spectroscopy to the study of these compounds is also associated with the modelling of processes occurring in protein molecules under corresponding conditions. In the present review we shall confine ourselves to a brief account of the possibilities of the infrared method for investigating the secondary structure of polypeptides.

The molecular chains in polypeptides exist mainly in one of three conformations—the α-helix, the β-conformation, or a coil[158-160]. X-Ray data indicate that one turn of the α-helix contains 3.6 amino-acid residues. The identity period along the axis of the helix is 27 Å. The height of one turn of the helix is 1.5 Å. An intramolecular hydrogen bond links amino-acid residues 1 and 3. The β-conformation is characterised by an almost completely extended polypeptide chain. Maximum saturation by intermolecular hydrogen bonds occurs when two polypeptide chains are mutually antiparallel. Owing to steric interaction of the β-carbon atoms, the peptide groups emerge from the plane of the carbon chain, and the polypeptide chains form so called folded layers having parallel and antiparallel arrangement of the chains. In the case of a folded layer having the chains parallel the identity period along the chain is 6.5 Å. The interchain period is 4.7 Å. The corresponding periods for a folded layer having antiparallel chains are 7.0 and 10 Å respectively.

The existence of a coiled conformation in polypeptide chains in appropriate solvents has been established from measurements of viscosity and optical rotation. Several polypeptides have been obtained in a coiled conformation in films, e.g. sodium polyglutamate and poly-*S*-carboxymethyl-L-cysteine[161,162]. The methods most widely used for investigating the secondary structure of polypeptide chains are optical rotation, X-ray diffraction, and infrared spectroscopy. Examination of the optical rotation of polypeptides will provide evidence of the presence of a helical conformation of the polypeptide chain in any solvent, but this method gives no information on other ordered conformations of polypeptides without special hypotheses. The X-ray method enables differences in the conformation of a polypeptide chain to be assessed fairly unambiguously, but it is too cumbersome and difficult for everyday use. Infrared spectroscopy began to be used to investigate the structure of polypeptides in the late 1940s and early 1950s. An empirical relationship was used between the conformation of a polypeptide chain and the position and dichroism of bands due to the peptide group



In practically all polypeptides except polyproline[158] the peptide group is in the planar *trans*-conformation[160,163]. This group has the characteristic absorption bands[164-167]—1650 (amide I), 1550 (amide II), 1300–1250 (amide III), 627 (amide IV), 720 (amide V), 600 (amide VI), and 200 (amide VII)—among which amide I and amide II are most often used for structural investigations. Some 80% of the potential energy associated with the amide I band is due to stretching vibrations of C=O groups, 10% is due to CN, and 10% to deformation vibrations of NH groups. Variation in the dipole moment of this oscillation occurs approximately in the direction of the C=O bond. The amide II vibration is 60% associated with deformation vibrations of NH and 40% with vibrations of CN. Variation in the dipole moment of this oscillation is perpendicular to the NH bond. To a first approximation the amide I and amide II vibrations are localised in the amide group, and are thus independent of the chemical structure of the polypeptide[167,168].

The position and polarisation of the amide I and amide II bands, as well as of the NH-stretching band, are given in Table 6 for various conformations of polypeptides[169].

Table 6.

Vibration	α-Helix	Dichroism	β-Form	Dichroism	Coiled
N-H stretching	3290—3330	∥	3280—3300	⊥	3400
Amide I	1650—1660	∥	1630	⊥	1660—1700
Amide II	1540—1550	⊥	1520—1530	∥	<1520?

An explanation has recently been put forward[170,171] for the observed difference in position and polarisation of the amide I and amide II absorption bands depending on the conformation of the polypeptide chain. Calculation of the dichroism and frequency positions of these bands in various conformations took into account the effect of interaction between amide I and amide II vibrations in neighbouring groups along the chain and between chains. Table 7 gives the results of such calculation, the symbols δ and δ' denoting the phase of the vibration in the adjacent amide group along the chain and between chains respectively.

The calculation[170,171] provides a good qualitative explanation of the dependence of the positions of amide I and amide II on the conformation of the polypeptide chain, but the numerical values thus obtained for the frequencies are not always correct. This is due mainly to the choice of unperturbed amide I and amide II vibrations.

Thus Krimm[172,173], unlike other workers[170], considers that the frequency 1520 cm^{-1}—not 1535 cm^{-1}—corresponds to the unperturbed amide II vibration. The value of ν_0 has been shown[174,175] to vary from 1659 to 1653 cm^{-1} for amide I, and from 1540 to 1566 cm^{-1} for amide II, which indicates that factors other than those connected with the conformation of the polypeptide chain influence the position of these frequencies. In this connection it should be noted that the

so-called coiled conformation of polypeptides may contain segments of chains in various states of order. Therefore values of ν_0 calculated from the infrared spectra of polypeptides in a coil are also not altogether correct. In order to determine the conformations of polypeptide chains it is most correct to use the frequency characteristic of the amide I and amide II bands together with measurements of their dichroism. Recently the amide V frequency, relating to out-of-plane vibration of NH, has begun to be used[176-178] to determine the conformation of polypeptide chains. This vibration is situated at 610–620, 700, and 650 cm^{-1} for the α-conformation, the β-conformation, and a coil. However, the degree to which this vibration is localised in the amide group is not altogether clear at the present time, since the positions of amide V for various conformations of the polypeptide chain have been studied on a relatively small class of polypeptides.

Table 7.

Conformation of polypeptide chain	Frequency assignment (δ, δ')	Amide I frequency		Amide II frequency	
		calc.	obs.	calc.	obs.
Coiled	ν_0	1658	1655 1650 s.	1535	1535
Helix	$\nu_{0\parallel}$	1650		1516	1516 w.
	$\nu_\perp$ $(2\pi/n)$	1647	1652 m.	1546	1546 s.
Folded-chain layer with parallel packing of chains	$\nu_\parallel$ (0, 0)	1648	1645 w.	1530	1530 s.
	$\nu_\parallel$ (π, 0)	1632	1630 s.	1550	1550 w.
Folded-chain layer with antiparallel packing of chains	$\nu_\parallel$ (0, 0)	1685	1685 w.	1530	1530 s.
	$\nu_\perp$ (π, 0)	1632	1632 s.	1540	—
	$\nu_\perp$ (π, π)	1668		1550	—

One of the chief perculiarities of polypeptides is the dependence of the conformation of their polypeptide chain on the nature of the solvent. Thus poly(γ-benzyl L-glutamate) has the α-helical conformation in chloroform solution, but passes into the coiled conformation in dichloroacetic or trifluoroacetic acid[179]. Use of the infrared absorption spectra to investigate the conformation of polypeptides in solution is difficult for two reasons: firstly, most solvents themselves absorb in the range investigated, and it is difficult to choose compensating conditions for such solvents as dichloroacetic and trifluoroacetic acids; on the other hand, as has already been noted, the amide I and amide II frequency characteristics do not always fully reflect the conformation of the polypeptide chain, and measurement of their dichroism in solution requires special apparatus[180,181].

At the present time it has not been accurately established what are the factors affecting formation of one or other conformation of polypeptides. Most authors link the conformation either with the molecular weight of the specimens[182-185] or with the type of amino-acid residue[186,187]. It has been shown experimentally and theoretically[188-190] that the α- and β-conformations are energetically close together. In working with polypeptides in the form of films, therefore, it must be borne in mind that the conformation of the polypeptide chain will depend in some cases on the nature of the solvent and also on other conditions of preparation of the specimen[183,184,189].

Measurement of the intensities of the amide I, amide II, and amide V absorption bands provides in principle a method for estimating quantitatively the presence of the α- and β-conformations and the coiled conformation in polypeptides. However, no accurate values are yet available for the absorption coefficients of these three amides in the various conformations. Preliminary results obtained by Blout and his coworkers[191,192] indicate that the absorption coefficients of corresponding amides are the same for the different conformations. The same conclusion has been reached from a study of the orientation of polypeptides[189].

Several polypeptides can exist under certain conditions in an ω-helical[193] conformation, as a 3_{10} helix[194], or as the so-called β-cross conformation[184,195-198]. Only the last of these three conformations has been well defined by means of infrared spectroscopy. A spectroscopic criterion of this conformation is provided by amide I and amide II frequencies characteristic of the β-structure and the dichroism observed in polypeptides present as α-helices. The positions of amide I and amide II in the spectrum of polypeptides in this conformation and their polarisation are explained by peculiarities in the packing of the polypeptide chain. The chains have a β-extended conformation coiled into the shape of bellows, individual units in which are joined by intramolecular hydrogen bonds. This structure recalls that of the polymer chain in a single crystal. The maximum information on the structure and conformation of the polypeptide chain can probably be obtained by investigating amide VII (200 cm^{-1}), but data on its position in the various conformations are not available at the present time, since the manufacture of standard apparatus for this spectral range started only recently.

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New Information about Oxygen-containing Compounds of Iodine

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1. INTRODUCTION

The systematic investigation of the oxygen-containing compounds of iodine has been carried out over the last 150 years but their study is far from complete. These compounds differ considerably from the compounds of the other halogens in their composition, nature of the bonding, stability, and other properties. Compared with chlorine and bromine, iodine forms a greater number of compounds, corresponding to the increased stability of the halogen–oxygen bond.

The following stable compounds are known in the solid state: I_2O_4, I_4O_9, I_2O_5, HIO_3, HI_3O_8, IO_3, HIO_4, $H_7I_3O_{14}$, H_5IO_6, and the salts of the acids mentioned. Furthermore, certain polyiodates are also known which have a composition other than that corresponding to tri-iodic acid HI_3O_8. As well as the oxide of composition IO_3 there are also salts which contain iodine(VI) corresponding in composition to the hypothetical acid H_2IO_4 or $H_2I_2O_7$. There have been descriptions of a series of salts which are derivatives of diperiodic acid $H_4I_2O_9$, the existence of which in the free state is disputed, and also salts of the hypothetical mesoperiodic acid H_3IO_5.

Information about the oxygen-containing compounds of iodine(V) and also about lower oxides of iodine is given in a series of well-known reviews and monographs on inorganic chemistry. Compounds of iodine(VI) and iodine(VII) have been less studied. Whilst orthoperiodic H_5IO_6 and metaperiodic HIO_4 acids and periodates of various compositions (derivatives of the acids H_5IO_6, H_3IO_5, HIO_4, and $H_4I_1O_9$) have long been known, the existence of triperiodic acid $H_7I_3O_{14}$, one of the products of the thermal decomposition of orthoperiodic acid, has only been shown recently. The oxide of composition IO_3 was recently isolated as a product of the thermal decomposition of periodic acid in a vacuum. Interesting results were also obtained in studying the thermal decomposition of periodates. These investigations led to the discovery of salts of the triperiodic acid mentioned above and of certain iodine(VI) compounds. The latter compounds, which contain iodine in an uncommon valence state also have the character of salts. Compounds of this type are completely unknown for the lighter homologues of iodine.

Recent investigations of the thermal decomposition of periodic acid and periodates have revealed extremely important information about the chemistry of iodine compounds. A considerable part of this review is devoted to this question.

2. LOWER OXIDES OF IODINE

The oxide of the empirical composition I_2O_4 is formed as a yellow powder on heating iodic acid with concentrated sulphuric acid and decomposing the sulphate first formed $(IO)_2SO_4$ with water[1-3]. This oxide is sparingly soluble in water and in organic solvents. At elevated temperatures with water it disproportionates to iodic acid and iodine. At higher temperatures I_2O_4 decomposes with the formation of iodine pentoxide and elemental iodine[4].

The oxide I_2O_4 is often considered as a compound of iodine of mixed valency (ter- and quinque-valent iodine). It is diamagnetic[5] and therefore it cannot be represented as the monomer IO_2. It must be considered as the dimer I_2O_4, or even as a polymer $(IO_2)_x$. Analysis of the infrared spectra indicate that the structure of this oxide in the solid state is a chain of

–O–I–O–I–O–

groups, with which a lattice of IO_3^- anions is bonded. Ideas[8] about the existence in the crystal lattice of simple iodyl cations and discrete molecules $(IO)^+(IO_3)^-$ seem incorrect.

The iodyl group is present in certain other iodine compounds, particularly salts (especially sulphates, selenates, and nitrates)[9,10].

An oxide of composition I_4O_9 is formed by the action of ozone on iodine (in the gas phase at 50°C or in solution in chloroform or carbon tetrachloride) as a yellow product[3,11-13]. By analogy with other iodine(III) salts this oxide is usually considered[14] as iodine iodate $I(IO_3)_3$.

3. IODINE(V) COMPOUNDS

Iodic acid HIO_3 is the most stable oxygen-containing acid of iodine. Together with iodates and iodine pentoxide it was known as early as the first half of the preceding century (Davy, 1815). Ever since, iodine(V) compounds have formed the subject of investigations by many authors.

The basis of the synthesis of iodic acid is oxidation of iodine by various reagents (for example, nitric acid, chlorine, by electrolysis, etc.) or by displacement of iodic acid from its salts by other acids. Iodates are obtained by neutralisation or even the oxidation of iodine in alkaline medium. Iodine pentoxide I_2O_5 can be made by the direct reaction of the constituent elements at elevated temperature or by dehydration of iodic acid (see below).

As well as simple iodates other derivatives of iodic acid, namely, a series of double salts and also salts with a complex cation, are known. For complexes in which iodate anions act as ligands, the preparation and properties of the acids $H_2[Sn(IO_3)_6]$, $H_2[Sn(OH)_2(IO_3)_4]$, and $H_2[Sn(OH)_4(IO_3)_2]$ and their salts have been investigated[15]. These compounds were obtained by the reaction, and subsequent crystallisation, of tin(IV) chloride (or potassium hexachlorostannate) with iodic acid (or with alkali metal iodates) in acid medium. Compounds of titanium(IV)[16], lead(IV)[17], manganese(IV)[18], and uranium(IV)[19] were isolated in a similar manner and investigated. Compounds of niobium and tantalum, have been described in which the iodine coordination number is 6. These can be represented by the formulae[20]: $Nb_2O_5.2HIO_3.2H_2O$ and $Ta_2O_5.HIO_3.6H_2O$.

Of the compounds which contain a cationic complex, there have been studies of certain iodate salts of hexamminecobalt(II), for example, $[Co(NH_3)_6](IO_3)_2.3H_2O$ [21], and of hexamminecobalt(III), for example, $[Co(NH_3)_6](IO_3)_3.3HIO_3$, also the iodates of hexammineplatinum(IV), of tetrammineplatinum(II), and tetramminepalladium(II).[22,23] The existence of certain simple iodate salts, their hydrates,, and in particular of a series of double compounds was established in a solubility study of multicomponent systems at various temperatures (Table 1).

Iodic acid is known in two modifications: α and β. Both are orthorhombic and differ only in the ratio of the crystallographic axes. Several early papers dealt with the structure of this compound[50-52]. Later only the α modification interested most authors[53-58]. The structure investigated consists of aggregates of molecules mutually connected by hydrogen bridges, which contain IO_3 groups in the form of deformed octahedra. There are 4 HIO_3 molecules in the unit cell. The presence of O–H–O bonds was confirmed also by the neutron diffraction method[59].

Several papers[51-53,60-66] are devoted to the study of the structure of iodates, particularly the alkali metal salts. These are usually compounds for which a perovskite lattice is characteristic, where the iodine has a coordination number of six. The perovskite-type compounds include potassium, rubidium, caesium, and ammonium iodates. It was found that as the atomic number of the cation is increased the edge of the lattice lengthens. The existence of a perovskite-type crystal lattice for these compounds was also established by the NMR method[67]. The structure of sodium iodate remained unexplained. Some authors assume that it has an antiperovskite-type structure[53,61,65]. For several other iodates, particularly those of silver, copper, calcium, barium, radium, and aluminium, the literature mentions only the system in which they are crystallised[51,52,60,68-72]. The structure of cerium(IV) iodate has been studied in greater detail[73,74]. Table 2 lists iodine(V) compounds, the structure of which has been investigated by X-ray diffraction.

Table 1. Equilibrium systems of compounds of iodine(V).

Equilibrium system	Compounds formed in the system	Reference
1	2	3
$HIO_3 - NH_3 - H_2O$	$NH_4H(IO_3)_2$; $NH_4H_2(IO_3)_3$	24
$HIO_3 - HNO_3 - H_2O$	$HIO_3 \cdot 2HNO_3$	25
$I_2O_5 - HF - H_2O$	$2HIO_3 \cdot 3HF$	26
$I_2O_5 - NaF - H_2O$		27
$I_2O_5 - KF - H_2O$	$KH(IO_3)_2 \cdot H_2O$; $KH(IO_3)_2 \cdot KF \cdot 4H_2O$	27
$NaIO_3 - HIO_3 - H_2O$	$NaIO_3 \cdot 2HIO_3$	28
$NaIO_3 - I_2O_5 - H_2O$	$Na_2O \cdot 2I_2O_5$; $NaIO_3 \cdot 1,5H_2O$	28
$NaIO_3 - NaI - H_2O$	$NaIO_3 \cdot 5H_2O$; $NaIO_3H_2O$	29
	$2NaIO_3 \cdot 3NaI \cdot 20H_2O$ (15; $10H_2O$)	30
	$3NaIO_3 \cdot 4NaI \cdot 23H_2O$	31
$NaIO_3 - NaCl - H_2O$	$2NaIO_3 \cdot 3NaCl \cdot 20H_2O$ (15; $10H_2O$)	30
$NaIO_3 - NaBr - H_2O$	$2NaIO_3 \cdot 3NaBr \cdot 15H_2O$ ($10H_2O$)	30, 42
$NaIO_3 - KIO_3 - H_2O$		32
$NaIO_3 - NaNO_3 - H_2O$	$2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$; $NaIO_3 \cdot H_2O$	34, 35
$NaIO_3 - NaClO_3 - H_2O$		36
$NaIO_3 - Na_2SO_4 - H_2O$	$NaIO_3 \cdot 3Na_2SO_4$; $NaIO_3 \cdot 4Na_2SO_4$	37
$NaIO_3 - Na_2CO_3 - H_2O$		38
$NaIO_3 - Na_2C_2O_4 - H_2O$		39
$NaIO_3 - Na_2MoO_4 - H_2O$		40
$KIO_3 - HIO_3 - H_2O$	$KIO_3 \cdot HIO_3$; $KIO_3 \cdot 2HIO_3$	28, 41
$KIO_3 - KCl - H_2O$		32
$KIO_3 - KBr - H_2O$		42
$KIO_3 - KI - H_2O$		31, 43
$KIO_3 - KNO_3 - H_2O$		44
$KIO_3 - KClO_3 - H_2O$		36
$KIO_3 - K_2SO_4 - H_2O$		32
$KIO_3 - K_2MoO_4 - H_2O$		45
$NH_4IO_3 - HIO_3 - H_2O$	$NH_4IO_3 \cdot 2HIO_3$; $NH_4IO_3 \cdot HIO_3$	28, 46
$AgIO_3 - M^IIO_3 - H_2O$ (M^I = Li, Na, K, NH_4)	$KIO_3 \cdot 2HIO_3$	47
$AgIO_3 - I_2O_5 - H_2O$	$AgIO_3 \cdot I_2O_5$	47
$Mg(IO_3)_2 - NaIO_3 - H_2O$	$Mg(IO_3)_2 \cdot 10H_2O(4H_2O)$; $NaIO_3 \cdot 5H_2O(H_2O)$	32
$Mg(IO_3)_2 - Mg(NO_3)_2 - H_2O$	$Mg(IO_3)_2 \cdot 10H_2O$	48
$Ca(IO_3)_2 - NaIO_3 - H_2O$	$Ca(IO_3)_2 \cdot H_2O$	44
$Ba(IO_3)_2 - BaCl_2 - H_2O$	$Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$	49

The structure of iodic acid and of its salts has been studied by various physical methods (mainly spectroscopic and magnetic) both in the solid state and in solution. The nature of the Raman and infrared spectra agrees with the idea that in the solid state and in highly concentrated solutions there is polymerisation of the HIO_3 molecules[75-90]. The presence of $(HIO_3)_3$ trimers is usually assumed but the possible existence of polymers of the type $H_2I_4O_{11}$ etc. has also been discussed[91]. The degree of polymerisation usually drops with decrease in the concentration of the acid in the solution. In dilute solutions there are simple IO_3^- anions. Fonteyne[92] suggests that molecules of the pseudo-acid $HO-IO_2$ are also present. Study of the spectra of

iodates[81,83,93-107] suggests a symmetrical pyramidal structure for the IO_3^- anions. The molecule of iodine pentoxide I_2O_5 is also constructed symmetrically: two IO_2 groups are connected by an oxygen atom[108]. Magnetic susceptibility measurements also support these ideas on the structure of iodic acid molecule and anion[109-119]. The investigation of other properties of iodic acid and the determination of certain physical constants has mainly given way to a tendency to prove the presence of polymerisation of the molecules in concentrated solutions[120-137].

By thermal decomposition of certain hydrated iodates a series of hydrates with less water, and anhydrous salts, were isolated, and the limits of their stability established[105,106,138-150]. Dehydration of iodic acid at elevated temperature[151,152], forms tri-iodic acid HI_3O_8:

$$3HIO_3 \rightarrow HI_3O_8 + H_2O.$$

Table 2. Results of the X-ray studies of the structure of iodine(V) compounds.

Composition of compound	Crystallographic system	Lattice parameters, Å	No. of molecules in unit cell	Interatomic distances	References
1	2	3	4	5	6
HIO_3	o-rh.	$a = 5.520$ $b = 5.855$ $c = 7.715$	4	I — O: 1,80—2,90 O—O: 2,78 H—O—H: 2,68	50, 53, 54, 55 57, 58, 59
$3I_2O_5 \cdot H_2O$	mon.	$a:b:c = 0,901:1:0.891$ $\beta = 112°53'$			154
$LiIO_3$	hex.	$a = 5.469$ $c = 5.155$ (4,05)	2	Li—O=I—O=2,33	61
$NaIO_3$	o-rh.	$a = 5.75$ $b = 6.37$ $c = 8.10$	4	I—O = 1,80; 2,84 (2,05; 2,08; 3,18)	53, 65, 66
KIO_3			4		60, 63, 64, 67, 69
$KH(IO_3)_2$	mon.				51, 52
$KH_2(IO_3)_3$	tric.				51, 52
$CsIO_3$					53, 67
NH_4IO_4	cub. or o-rh.?	$a = 6.41$ $b = 6.38$ $c = 9.25$			62, 65
$AgIO_3$	o-rh.				60
$Cu(IO_3)_2$	mon.				68
$Cu(IO_3)_2 \cdot H_2O$	tric.				68
$Mg(IO_3)_2 \cdot 4H_2O$	mon.				68
$Ca(IO_3)_2$	mon.	$a = 7.18$ $b = 11.38$ $c = 7.32$ $\beta = ?$			69
$Ca(IO_3)_2 \cdot 6H_2O$	o-rh.				51, 52
$Ba(IO_3)_2$	mon.				70
$Sr(IO_3)_2$	tric.				70
$Al(IO_3)_2 \cdot NO_3 \cdot 6H_2O$	trig.				72
$Ce(IO_3)_4 \cdot H_2O$	mon.	$a = 9.57$ $b = 14.92$ $c = 8.00$ $\beta = 97°35'$	4		73, 74

This acid can also be obtained by recrystallisation of iodic acid from concentrated nitric acid. Some authors ascribe the formula $3I_2O_5 \cdot H_2O$ to this compound[153-156]. Oxygen bridges were indicated in the HI_3O_8 molecule by infrared spectra[91,157]. The existence of other transitional hydrates, as, for example, $2I_2O_5 \cdot H_2O$, was not confirmed. According to some results the dehydration of iodic acid takes place directly with the formation of iodine pentoxide[158,159]. Some differences have been observed[160] in the dehydration of the α and β modifications of HIO_3.

By heating an equimolar mixture of potassium (or rubidium) iodate and iodine pentoxide in a sealed ampoule at 170°C, and also by the dehydration of salts of the type $M^IH_2(IO_3)_3$, the salts of tri-iodic acid KI_3O_8 and RbI_3O_8 can be obtained[161]. However, the formation of potassium triiodate in the thermal decomposition of $KH(IO_3)_2$ was not observed[152]—here only a mixture of the iodate and iodine pentoxide is formed.

The structure of the acid iodates and the question of the polymerisation of iodic acid and iodates are still unsolved problems. The acid iodates $M^IH(IO_3)_2$ and $M^IH_2(IO_3)_3$ can be obtained by crystallisation from aqueous solution of an equimolar mixture of iodate and iodic acid. According to early ideas they can be considered[162-165] as double compounds of general formula $M^IIO_3 \cdot HIO_3$ or $M^IIO_3 \cdot 2HIO_3$. The existence of such compounds is confirmed by equilibrium diagrams of multicomponent systems (see Table 1). Starting from the behaviour of iodic acid in solution, its dimer

Table 3. Spectroscopic investigations of iodine(V) compounds.

Compound	Spectroscopic method	Reference	Compound	Spectroscopic method	Reference
I_2O_5	IR	108, 157	$Sr(IO_3)_2 \cdot H_2O$	IR	105, 106
HIO_3	IR	86, 104, 157	$Sr(IO_3)_2$	RS	100
	RS	75—88, 92, 95	$Ba(IO_3)_2 \cdot H_2O$	IR	105, 106
HI_3O_8	RS	91	$Zn(IO_3)_2$	IR	105, 106
$LiIO_3$	IR	105	$Cd(IO_3)_2$	IR	105, 106
	RS	77, 81	$Ni(IO_3)_2$	IR	104, 105, 106
$NaIO_3 \cdot H_2O$	IR	105, 157	$Co(IO_3)_2$	IR	104, 105, 106
	RS	98	$Pb(IO_3)_2$	IR	104, 105, 106
KIO_3	IR	7, 105, 157	$Mn(IO_3)_2$	IR	104
	RS	83, 84, 95	$Fe(IO_3)_3$	IR	104
	X-ray abs. spectra	99	$Th(IO_3)_4$	IR	104
$KIO_3 \cdot HIO_3$	RS	77	$Hg_2(IO_3)_2$	IR	104
	IR	104	$Hg(IO_3)_2$	IR	104
M^IIO_3 (M^I = alkaline metal)	IR	97, 104, 106	$K_2Mn(IO_3)_2$	IR	7, 104
	RS	77, 94, 96, 103, 107	$K_2Pb(IO_3)_6$	IR	104
	UV	101, 102, 137	$K_2Ti(IO_3)_6$	IR	104
$AgIO_3$	IR	104, 105, 106			
$Mg(IO_3)_2 \cdot 4H_2O$	IR	105, 106			
$Ca(IO_3)_2 \cdot 6H_2O$	IR	105, 106			

* IR = infrared absorption spectra; RS = Raman spectra; UV = ultraviolet spectra.

is often considered a dibasic acid and the presence of the anion $I_2O_6^{2-}$ in solution has been suggested[77,92,122,135,166]. In other studies the existence of such an anion has been denied[167,168]. Polyiodates of the type $K_2H_2I_6O_{17}$ and $K_2I_4O_{11} \cdot 2H_2O$ have also been obtained by the thermal decomposition of certain hydrogen iodates. Infrared spectroscopy showed[157] the presence of I—O—I bridges in these polyiodates. Table 3 lists the compounds of iodine(V) the structure of which has been studied by spectroscopic methods.

Iodine dioxide fluoride IO_2F is also an iodine(V) compound. It can be obtained[169] by the action of iodine pentoxide on iodine(V) fluoride or the action of fluorine on iodine pentoxide in anhydrous [hydrogen] fluoride[170]. IO_2F tends to form complexes, for example, the complex arsenate $IO_2[AsF_6]$.

4. THE OXIDE I_2O_7

The existence of the oxide I_2O_7 in the free state cannot be considered as definitely proved. In many attempts to make this substance compounds of another composition were obtained. The following were erroneously taken for the oxide I_2O_7: the product of the reaction of iodine with

oxygen or ozone under the action of a silent discharge[171], the product of the reaction of iodine with chlorine(VII) oxide[172,173], or even the product of the reaction of iodine with iodic acid[174]. Neither could periodic anhydride be obtained by the thermal decomposition of the iodic acid at various temperatures in air or in a vacuum[175]. As a result of the dehydration of orthoperiodic acid by gaseous fluorine[176] only the metaperiodic acid HIO_4, and not periodic anhydride, is formed. Even the metaperiodic acid could not be dehydrated completely by fluorine in anhydrous hydrogen fluoride. As a result of this reaction the iodine(VII) oxide fluoride IO_3F is formed[172]. The most successful was apparently an attempt[177] to dehydrate periodic acid in 65% oleum. The composition of the strongly reactive orange compound obtained differs little from the ultimate analysis of the oxide I_2O_7.

5. PERIODIC ACID

Four solid hydrates of iodine(VII) oxide are known: $I_2O_7.5H_2O$ (H_5IO_6, orthoperiodic acid), $3I_2O_7.7H_2O$ ($H_7I_2O_{14}$, triperiodic acid), $I_2O_7.2H_2O$ ($H_4I_2O_9$, diperiodic acid) and $I_2O_7.H_2O$ (HIO_4 metaperiodic acid).

a. Orthoperiodic acid H_5IO_6 has been known for about 130 years and methods for its preparation and principal chemical properties have been given in well-known monographs. This acid can be prepared by electrolysis[178] or by its displacement from periodates by the action of strong acids (particularly by use of nitric[179] and perchloric[180] acids). Orthoperiodic acid forms the starting point for making all the hydrates of the oxide I_2O_7 poorer in water. As a rule this is done by thermal decomposition of orthoperiodic acid at ordinary pressure or in a vacuum.

Periodic acid can be represented as the ortho-acid H_5IO_6 or as the dihydrate of the meta-acid $HIO_4.2H_2O$. The second formula was proposed on the basis of magnetic measurements[181] according to which the experimental magnetic susceptibility of periodic acid ($\chi = -71.4 \times 10^{-6}$) is close to the value calculated for the dihydrate $HIO_4.2H_2O$ ($\chi = -77.7 \times 10^{-6}$) and slightly different from the value calculated for orthoperiodic acid ($\chi = -55.7 \times 10^{-6}$). Other authors who studied the dehydration of periodic acid in anhydrous pyridine[182] also consider periodic acid to be the dihydrate of the meta-acid. However, the structural measurements show that it is more correct to consider the pentahydrate of the oxide I_2O_7 to be the ortho-acid. The Raman spectrum of periodic acid in the solid state shows the octahedral symmetry of the IO_6 group. In the spectrum of the aqueous solution of periodic acid four lines agree with the frequencies of the metaperiodate anion IO_4^- and three lines correspond with the undissociated H_5IO_6 molecules. It is therefore assumed[183] that in solution the ortho-acid undergoes dehydration:

$$H_5IO_6 \rightleftarrows H^+ + IO_4^- + 2H_2O.$$

In the absorption spectra of periodic acid in the infrared region distinct bands can also be distinguished at 2900 and 2200 cm^{-1}, due to the OH group, and in the 1100–1300 cm^{-1} range there are bands due to the I–OH groups, whereas the bands at 3400 cm^{-1}, typical for water molecules, are absent.

The octahedral structure of the anion IO_6^{5-} also follows from the structure found for orthoperiodic acid[185,186]. This compound is monoclinic with somewhat deformed octahedra of oxygen atoms about the central iodine atoms. Since conclusions based on the direct determination of structure by spectroscopic and X-ray diffraction methods ought to be considered more reliable than those which follow from magnetic measurements and dehydration experiments, it can be assumed that the correct formula for the pentahydrate of I_2O_7 is H_5IO_6, that is, this compound is the ortho-acid.

By heating the orthoperiodic acid in the atmosphere it loses water and is converted into triperiodic and then metaperiodic acid. Above 170°C it undergoes more extensive decomposition into iodine(VII) oxide[187]. The thermal decomposition of this acid in a vacuum is somewhat more complex (see below).

b. Triperiodic acid $H_7I_3O_{14}$ is formed[187] as a primary dehydration product as a result of the thermal decomposition of orthoperiodic acid in the temperature range 121-130°C. This compound was discovered in an attempt to reproduce the diperiodic acid preparation according to Partington and Bahl[188]. The existence of triperiodic acid was proved by thermogravimetric, tensimetric, and X-ray diffraction methods[187]. The decrease in the weight of the specimen observable in the thermogravimetric study of the dehydration of some preparations of orthoperiodic acid (prepared by three different methods) is always less than would correspond with the formation of diperiodic acid. Instead of the expected 1.5 moles water which correspond with the formation of diperiodic acid, the observed loss in weight during the dehydration amounts to 1.33 moles water per 1 mole of the initial acid. Therefore the dehydration can be represented by the equation:

$$3H_5IO_6 = H_7I_3O_{14} + 4H_2O.$$

The formation of triperiodic acid was also confirmed by dehydration in a vacuum on a quartz spiral thermobalance at 60°C. The tensimetric measurements made by Hauptman[187] refute the incorrect conclusions of Partington and Bahl[188] concerning the existence of diperiodic acid $H_4I_2O_9$. The measurements of the latter authors were insufficiently detailed, since they did not record experimental points in the range important for deciding to which composition the break on the tensimetric curve relates ($H_4I_2O_9$ or $H_7I_3O_{14}$).

c. Diperiodic acid $H_4I_2O_9$. The existence of diperiodic acid in the solid state has been noted in only two studies. The first of these is the work of Partington and Bahl already mentioned[188], in which tensimetric measurements were made. As we have already noted, the results obtained by these authors were later refuted by Hauptman[187].

Ripanova and Duca[189] described the isolation of diperiodic acid from aqueous solution. The acid was displaced from barium diperiodate by the action of sulphuric acid of from the silver salt by the action of hydrogen chloride. The acid was separated by crystallisation from the solution obtained. The authors also propose the formation of diperiodic acid in solution, in which orthoperiodic and metaperiodic acids are present in 1 : 1 ratio. From conductometric measurements the authors assume that this acid should be formed on the introduction of carbon dioxide into a solution of orthoperiodic acid. Diperiodic acid should be precipitated, since its solubility is only about one-sixtieth of that of the ortho-acid. However, Hauptman[187] did not succeed in reproducing these extremely unreliable results.

d. Metaperiodic acid HIO_4 was first obtained[190] by dehydrating orthoperiodic acid at reduced pressure at 100°C. Later the formation of this acid was also confirmed by other authors, who investigated the thermal decomposition of the ortho-acid in the air[188,191] in the tem-

perature range 140–170°C and in vacuum[192] at 80°C. Furthermore, it was shown that the sublimate formed as a result of the dehydration of the ortho-acid at reduced pressure is metaperiodic acid. Proof was obtained by the ultimate analysis and by comparison of the X-ray powder patterns of the sublimate and metaperiodic acid[191,193].

Both the well-known hydrates poorer in water, that is, the acids $H_7I_3O_{14}$ and HIO_4, are extremely hygroscopic compounds and therefore they are instantaneously rehydrated to the ortho-acid with atmospheric moisture.

e. The oxide IO_3. In the thermal decomposition of orthoperiodic acid in a vacuum two processes take place in the range 105–117°C: decomposition and simultaneous sublimation. On the colder parts of the apparatus a deposit is formed which according to earlier publications contains only iodine(VII) and is in all probability metaperiodic acid. A yellow substance containing formally sexivalent iodine remains at the bottom of the decomposition tube. According to the ultimate analyses its composition corresponds to the formula IO_3. The X-ray diffraction pattern of the powder also shows the individuality of the compound IO_3. The lines of the powder pattern of the substance were compared with those for HIO_4, I_2O_5, and HI_3O_8. The oxide IO_3 is formed[193] also in the thermal decomposition of the lower hydrates of iodine(VII) oxide ($H_7I_3O_{14}$ and HIO_4) in a vacuum at 115°C. However, the appearance of the sublimate formed by the decomposition of these compounds differs from that of the sublimate obtained in the decomposition of orthoperiodic acid. Because of experimental difficulties (mainly the considerable rehydration of the sublimate under the action of the water liberated) the composition of this product cannot be determined accurately nor is it possible to show whether the decomposition of the lower hydrates of iodine(VII) oxide results in the formation of metaperiodic acid or the anhydrous oxide I_2O_7.[192]

6. SALTS OF PERIODIC ACID

Periodates were discovered[194] in 1833 in the oxidation of a mixture of iodine and sodium carbonate solution with chlorine. Oxidation of various iodine compounds with chlorine in alkaline medium is themain method of preparing alkali metal periodates. Periodates of other metals are obtained from these by double decomposition in aqueous medium (by precipitation). Almost all the known periodates can be divided into four classes according to their composition: the metaperiodates M^IIO_4; mesoperiodates $M^I_3IO_5$ or $M^I_2HIO_5$; the orthoperiodates $M^I_2H_3IO_6$, $M^I_3H_2IO_6$, and $M^I_5IO_6$; and the diperiodates $M^I_4I_2O_9$. In some earlier studies[175,195], periodates of another composition are considered, for example, $M^I_8I_2O_{11}$, etc. Probably the authors isolated basic salts or even mixtures of the metal oxides and the corresponding periodates.

The investigation of the periodates is directed mainly to the preparation of new compounds and the subsequent study of their structure and physical properties. Several papers are also devoted to the investigation of their thermal decomposition.

The preparation of new simple periodates has usually accompanied the detailed study of the metal oxide–iodine(VII) oxide–water ternary system. The formation of new compounds in the ternary systems were established from the solubility curve or from measurements of the pH, etc. With the aid of such a method there has been success in extending considerably the number of known simple and double periodates of lithium[196,197], sodium[198,199], potassium[198,200], beryllium[201], magnesium[202], calcium and barium[203], lead(II)[204], copper(II)[205], silver[206–208], cadmium[209], and iron(III)[210] and observing all the periodates of the corresponding metals which can exist in the range of temperature studied in the presence of water. The systems studied are listed in Table 4.

Table 4. Equilibrium systems of iodine(VII) compounds.

Equilibrium system	Compounds formed in the system	Reference
$Li_2O—I_2O_7—H_2O$	Li_5IO_6, $Li_3H_2IO_6$, $Li_2H_3IO_6$, $LiIO_4 \cdot H_2O$	196
$Li_2H_3IO_6—(NH_4)_2H_3IO_6—H_2O$	$NH_4LiHIO_6 \cdot 3\,H_2O$	197
$NaIO_4—NaOH—H_2O$	$NaIO_4 \cdot 3\,H_2O$, $Na_2H_3IO_6$, $Na_3H_2IO_6$	198
$Na_2H_3IO_6—(NH_4)_2H_3IO_6—H_2O$		199
$KIO_4—KOH—H_2O$	$K_4I_2O_9$, $K_4I_2O_9 \cdot 9\,H_2O$	198
$K_4I_2O_9 \cdot 9\,H_2O—H_2O—(NH_4)_2H_3IO_6$	$KNH_4H_3IO_6$	200
$Be(OH)_2—H_5IO_6—H_2O$	$Be_5(IO_6)_2 \cdot 12H_2O$; $Be(IO_4)_2 \cdot 13\,H_2O$	201
$Mg(OH)_2—H_5IO_6—H_2O$	$Mg_5I_2O_9 \cdot 13\,H_2O$; $Mg(IO_4)_2 \cdot 8H_2O$	202
$Ca(OH)_2—H_5IO_6—H_2O$	$Ca_3(IO_5)_2 \cdot 9\,H_2O$; $Ca_2I_2O_9 \cdot 9\,H_2O$ $Ca(IO_4)_2 \cdot 6\,H_2O$	203
$Ba(OH)_2—H_5IO_6—H_2O$	$Ba_3(IO_5)_2 \cdot 2H_2O$; $Ba_2I_2O_9 \cdot 6\,H_2O$ $Ba(IO_4)_2 \cdot 6\,H_2O$	203
$Pb_3(IO_5)_2 \cdot H_2O—H_5IO_6—H_2O$	$Pb_2I_2O_9 \cdot 3\,H_2O$	204
$Pb_3(IO_5)_2 \cdot H_2O—KOH—H_2O$	$Pb_4I_2O_{11} \cdot 5\,H_2O$	204
$Cu(ClO_4)_2—NaIO_4—NaOH—H_2O$	$Cu_3HIO_6 \cdot 3\,H_2O$, $Cu_5(IO_6)_2 \cdot 5\,H_2O$ $NaCu_3IO_6$	205
$Ag_2O—I_2O_7—H_2O$	Ag_5IO_6, Ag_3IO_5, Ag_2HIO_6, $Ag_2H_3IO_6$ $AgIO_4$, $AgIO_4 \cdot 2H_2O$	206, 207 208
$Cd_5(IO_5)_2 \cdot 3{,}5\,H_2O—H_5IO_6—H_2O$	$Cd(IO_4)_2 \cdot 8\,H_2O$; $Cd_2I_2O_9 \cdot 13\,H_2O$	209
$Fe_2(SO_4)_3—KIO_4—H_2O$	$Fe_5(IO_6)_3$	210

There is considerable interest in those ammonium and alkali metal periodates which can be obtained[211] from aqueous solutions (primarily by precipitation with methanol or by crystallisation at 0°C). These are mainly mesoperiodates, which apparently contain five-coordinate iodine. They are of low stability and are readily converted into the corresponding orthoperiodates with apparently six-coordinated iodine (Table 5).

However, certain orthoperiodates of the $M^I_5IO_6$ type—for example, Na_5IO_6,[212,213] $Ca_5(IO_6)_2$, and $Ba_5(IO_6)_2$[175,203]—can be prepared only by "dry" methods, since in contact with water they undergo partial hydrolysis with the formation of periodates which have a lower metal : iodine ratio.

In the preparation of new periodates special attention has been paid to the investigation of compounds which contain an anionic complex with a metal atom of higher valency as central atom and periodate anions as ligands Mn^{IV}, Fe^{III}, Co^{III}, Ni^{IV}, Cu^{III}, Ag^{III}, and Ce^{IV} are encountered as central atoms in these compounds (the periodate ions stabilise the higher oxidation state of the metal, which is of low stability). In most instances the sodium, potassium, and barium salts of the following hypothetical acids have been obtained:

$H_{11}Mn(IO_6)_3^{214,215}$, $HMnIO_6^{216}$,
$H_2FeIO_6^{217,218}$, $H_3Fe_4(IO_6)_3$, $H_7Fe(IO_6)_3^{219}$,
$H_3Co_4(IO_6)_3^{220,221}$, $H_7Co(IO_6)_2^{215,222}$.
$HNiIO_6^{223}$,
$H_7Cu(IO_6)_2^{224,225}$,
$H_7Ag(IO_6)_2^{226}$,
$H_6Ce(IO_6)_3^{227}$,

The general method of preparing these compounds[228] consists in the addition of an appropriate oxidant (for example, hypochlorite or peroxodisulphate) to a slightly

acid solution of alkali metal periodate and the corresponding salt of the metal to form the central atom, then making the mixture alkaline. Sometimes the crystallisation of the complexes can be brought about by addition of alcohol. The oxidation state of the central metal atom was found by titration with a suitable reductant or by measuring the magnetic susceptibility. These compounds are usually coloured and readily soluble in water. They are more stable in alkaline medium but some of them retain their stability in acid. For example, the free acid $H_7Co(IO_6)_2$ is stable in aqueous solution and it can be obtained by passing a solution of the sodium salt through a suitable cation-exchange resin.

Other complexes with the character of heteropolyacids are more stable in acid medium. They include chiefly compounds of periodic acid with vanadium[229], niobium, and tantalum[20] pentoxides. In these compounds, which contain an anionic complex, the iodine plays the part of central atom and the ligands are oxygen or oxo-anions of the Group Vb elements.

Periodates with a complex cation, the central atom of which is an atom of a metal with a strongly expressed complex-forming ability (for example, Co^{III},[230-233] Cr^{III},[234,235] Pd^{II}, Pt^{II}, Pt^{IV} [23]), are also well known. The ligands most frequently encountered are NH_3 molecules, molecules of organic compounds, Cl^-, Br^-, and SCN^- ions, etc. Periodate anions usually do not enter the coordination sphere of these compounds.

The structure of periodates has been investigated by X-ray diffraction, especially for alkali metal and silver periodates. Table 6 surveys the published information[236-254]. Clearly, most of the anhydrous periodates are tetragonal. They are isostructural with scheelite and their anions form tetrahedra, whereas in the structure of orthoperiodates the IO_6^{5-} anions are arranged in octahedra. The diperiodate anions are also usually made up of two octahedra with one edge in common (that is, two oxygen atoms).

The structure of the ammonium and alkali metal periodates was also studied with the aid of spectroscopic methods. The infrared spectra led to some unexpected results. It was found, for example, that the structure of certain compounds which were thought earlier to be diperiodates or orthoperiodates corresponds to mesoperiodates[184,211]. Table 7 gives the results of these measurements. The infrared spectra of silver periodates[255] and some transition metal periodates[215] were studied rather more systematically.

Table 5. Metastable periodates and their conversion into stable compounds.

Metastable	Stable
$Li_2HIO_5 \cdot 8(4)\,H_2O$	$Li_2H_3IO_6$
$Li_3IO_5 \cdot Li_2HIO_5 \cdot 11\,H_2O$	$Li_2H_3IO_6 + Li_3H_2IO_6$
$Na_2HIO_5 \cdot 4\,H_2O$	$Na_2H_3IO_6$
$Na_3H_2IO_6 \cdot H_2O$	$Na_2H_3IO_6$
$Na_3IO_5 \cdot Na_2HIO_5 \cdot 14\,H_2O$	$Na_2H_3IO_6 + Na_3H_2IO_6$
$(NH_4)_2HIO_5$	$(NH_4)_2H_3IO_6$
$KNH_4HIO_5 \cdot H_2O$.	$KNH_4H_3IO_6$

Table 7. Composition of periodates corresponding to the results of spectroscopic measurements.

Periodates	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+
Meta-		$NaIO_4$	KIO_4	NH_4IO_4	$RbIO_4$	$CsIO_4$
Meso-	$Li_2HIO_5 \cdot 8\,H_2O$ $Li_2HIO_5 \cdot 4\,H_2O$ $Li_3IO_5 \cdot H_2O$ $Li_3IO_5 \cdot Li_2HIO_5 \cdot 11\,H_2O$	$Na_2HIO_5 \cdot 4\,H_2O$ $Na_3IO_5 \cdot Na_2HIO_5 \cdot 14\,H_2O$	$K_2HIO_5 \cdot 4\,H_2O$	$(NH_4)_2HIO_5$ $LiNH_4HIO_5 \cdot 3\,H_2O$ $KNH_4HIO_5 \cdot H_2O$		
Ortho-		$Na_2H_2IO_6 \cdot H_2O$	$K_2H_2IO_6 \cdot 3H_2O$ $K_5IO_6 \cdot 5.5\,H_2O$	$KNH_4H_3IO_6$		

Table 6. Results of the X-ray diffraction investigation of the structure of periodates.

Composition	Crystallographic system	Lattice parameters, Å	No. of molecules in unit cell	Interatomic distance	Reference	Note
$LiIO_4 \cdot 3\,H_2O$	tric.	$a = 6.13$; $\alpha = 93°28'$ $b = 9.43$; $\beta = 107°17'$ $c = 5.01$; $\gamma = 96°16'$	2		236	
$Li_2H_3IO_6$	hex.	$a = 5.31$ $c = 4.61$	1		236	
$NaIO_4$	tetrag.	$a = 5.322$ $c = 11.93$	1		237	
KIO_4	tetrag.	$a = 8.13$ $c = 12.63$			238	
$K_4I_2O_9 \cdot 9\,H_2O$	tric.	$a = 7.06$; $\alpha = 97°47'$ $b = 10.57$; $\beta = 121°30'$ $c = 7.56$; $\gamma = 81°55'$	1	I—I=2.7	239, 240 241	$\left[(OH)O_3I\langle O \rangle IO_3(OH)\right]^{4-}$
$KNH_4H_3IO_6$	mon.	$a = 6.300$; $\beta = 76°14'$ $b = 15.19$ $c = 6.813$	4		242	
$(NH_4)_2H_3IO_6$	hex.	$a = 6.88$ $c = 11.10$		I—O=1.93	243, 244	
$N(CH_3)_4IO_4$	tetrag.	$a = 8.77$ $c = 12.07$			245	
$Al(IO_4)_3 \cdot 12\,H_2O$	cub.	$a = 15.42$	8		246	octahedra IO_6^{5-} and $[Al(H_2O)_6]^{3+}$
$Na_3KH_3Cu(IO_6)_2 \cdot 14\,H_2O$	mon.	$a = 6.12$ $b = 14.84$; $\gamma = 97°38'$ $c = 25.18$	4	I—I=5.84 Cu—I=2.92	247	
$AgIO_4$	tetrag.	$a = 5.37$ $c = 12.07$	4		245, 248	
$Ag_2H_3IO_6$	hex.	$a = 5.31$ $\alpha = 67°38'$	1		249, 250 251	
Ag_2HIO_5					252	
$Na_7H_4Mn(IO_6)_3$	mon.	$a = 16.00$ $b = 19.57$ $c = 10.29$	4	I—Mn=2.97 I—O=1.95 Mn—O=1.90	253, 254	

The structure of periodates has also been determined on the basis of measurements of magnetic properties, especially, magnetic susceptibility[256-259]. The results of these measurements have sometimes enabled complexes to be distinguished from simple compounds.

Ammonium and silver trihydrogen periodates $(NH_4)_2H_3IO_6$ and $Ag_2H_3IO_6$ exhibit anomalous dielectric constants at low temperatures. This can be explained by a transformation to an antiferroelectric phase at low temperatures[244,260-265].

7. BEHAVIOUR OF PERIODATES AT ELEVATED TEMPERATURE

The thermal decomposition of periodates of various compositions is accompanied by loss of water, oxygen, and iodine (in some instances of only one or two of these components). Depending on the composition of the initial periodates, the products of their thermal decomposition are: partly dehydrated periodates, for example[197]:

$$3\,[LiIO_4\cdot 3H_2O]=Li_3H_4I_3O_{14}+7H_2O\,, \qquad (1)$$

or completely dehydrated periodates[200]:

$$K_4I_2O_9\cdot 9H_2O=K_4I_2O_9+9H_2O\uparrow\,, \qquad (2)$$

periodates of another composition, for example[197]:

$$3\,[(NH_4)_2\,Li_2I_2O_9\cdot 7H_2O]=2Li_3\,(NH_4)_2H_2I_3O_{14}+2NH_3+20\,H_2O\,, \qquad (3)$$

or[269]:

$$5Ba\,(IO_4)_2=Ba_5\,(IO_6)_2+4I_2+14O_2\,, \qquad (4)$$

compounds of iodine(VI), for example[270]

$$Na_2H_3IO_6=Na_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,, \qquad (5)$$

iodates[199]:

$$NaIO_4=NaIO_3+\frac{1}{2}\,O_2\,, \qquad (6)$$

or iodides[199]:

$$NaIO_4=NaI+2O_2\,. \qquad (7)$$

In the thermal decomposition of heavy metal periodates, oxides of the corresponding metal[271] or the metal in an elemental state[266,268] can also be formed.

Whereas the products formed as a result of the thermal decomposition of periodates according to Eqns. (2), (4), (6), and (7) are known substances and their formation during the course of these reactions was established long ago, the products obtained as a result of reactions (1), (3), and (5) were identified only recently. According to Eqn. (1), and also (3), in the thermal decomposition of periodates, periodates are formed which on the basis of their composition could be classified as salts of triperiodic acid $H_7I_3O_{14}$ obtained by Hauptman[187]. The substance produced in the partial dehydration of magnesium periodate[202] may also belong to these polyperiodates:

$$Mg\,(IO_4)_2\cdot 8H_2O=Mg\,(IO_4)_2\cdot 1.66\,H_2O+6.33\,H_2O\,,$$
$$3\,[Mg\,(IO_4)_2\cdot 1.66\,H_2O]=Mg_3\,(H_4I_3O_{14})_2\cdot H_2O\,. \qquad (8)$$

Since the structure of triperiodic acid and its salts has not yet been established, it is impossible to explain why triperiodates are formed as a result of the decomposition of periodates of metals of small ionic radius (Li^+, Mg^{2+}).

It was observed recently that iodine(VI) compounds are formed in the thermal decomposition of periodates at 200°C according to the equations:

		Reference
$Li_2H_3IO_6=Li_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,,$	(9)	272
$Na_2H_3IO_6=Na_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,,$	(10)	270
$Be_3\,(IO_5)_2\cdot 12H_2O=Be_3I_2O_9\cdot 4H_2O+8\,H_2O+\frac{1}{2}\,O_2\,,$	(11)	273
$Mg_2I_2O_9\cdot 2{,}5\,H_2O=2\,[MgIO_4\cdot 0{,}5\,H_2O]+\frac{3}{2}\,H_2O+\frac{1}{2}\,O_2\,,$	(12)	202
$Ca_2I_2O_9\cdot 9\,H_2O=2CaIO_4\cdot H_2O+7H_2O+\frac{1}{2}\,O_2\,,$	(13)	274
$Ba_2I_2O_9\cdot 9\,H_2O=2BaIO_4\cdot H_2O+7H_2O+\frac{1}{2}\,O_2\,,$	(14)	269
$2Al\,(IO_4)_3\cdot 12\,H_2O=Al_2\,(I_2O_7)_3\cdot 2H_2O+22\,H_2O+\frac{3}{2}\,O_2\,,$	(15)	275
$Pb_2I_2O_9\cdot 3H_2O=2PbIO_4+3H_2O+\frac{1}{2}\,O_2\,,$	(16)	271
$2Cd_2I_2O_9=4CdIO_4+O_2\,.$	(17)	209

The products of these reactions, which contain iodine(VI), are white or yellow. Most of them are stable over a wide range of temperatures (see Table 8). These compounds are stable in air in the absence of moisture but they react with water to form a mixture of iodic and periodic acids, iodates and periodates. For example, the compound Na_2IO_4 disproportionates in water to form the soluble iodate and insoluble periodate[270] according to Eqn. (18):

$$2Na_2IO_4+H_2O=NaIO_3+Na_3H_2IO_6\,. \qquad (18)$$

Table 8. Thermal stability of iodine(VI) compounds.

Compound	Temperature of formation, °C	Decomposition temperature, °C
Li_2IO_4	180	450
Na_2IO_4	180	370
$Be_3I_2O_9\cdot 4\,H_2O$	150	170
$CaIO_4\cdot H_2O$	180	370
$BaIO_4\cdot H_2O$	220	380
$MgIO_4\cdot 0{,}5\,H_2O$	220	380
$PbIO_4$	220	400
$Al_2(I_2O_7)_3\cdot 2\,H_2O$	90 *	

* In a vacuum at constant temperature.

Table 9. Values of the magnetic susceptibility and magnetic moments of iodine(VI) compounds.

Compound	$10^6\chi$	μ, μ_B
Li_2IO_4	+0.24	0.50
Na_2IO_4	+0.64	0.71
$Be_3I_2O_9\cdot 4\,H_2O$	+4.25	1.63
$CaIO_4\cdot H_2O$	+4.31	1.65
$BaIO_4\cdot H_2O$	+5.21	2.12
$MgIO_4\cdot 0{,}5\,H_2O$	+0.94	0.60
$PbIO_4$	+2.33	1.54
$Al_2(I_2O_7)_3\cdot 2\,H_2O$	+0.17	0.51

† It is impossible to consider as definitely solved the problem whether the dehydration of silver periodate $Ag_4I_2O_9.3H_2O$ (which is usually considered to be the orthoperiodate $Ag_2H_3IO_6$) proceeds by a similar reaction or decomposes more extensively with the liberation of oxygen[266-268].

8. CHARACTERISATION OF IODINE(VI) COMPOUNDS[202-209,269-275]

Although the products of the thermal decomposition of periodates correspond in composition to compounds containing iodine(VI) it could be assumed that they are equimolar mixtures of iodates and periodates or of iodates and peroxides. The latter possibility can be ruled out since the absence of peroxides from these products has been verified by a chemical method and, moreover, it was found that the products react with water to form iodates and periodates. Since peroxide is incapable of oxidising iodate to periodate under any circumstances, the substance which contains the formally sexivalent iodine cannot be a mixture of iodates and peroxides. The problem of whether the thermal decomposition products of periodates are chemical individuals or mixtures of iodates and periodates was solved successfully by magnetic susceptibility measurements. Important results were also obtained by X-ray diffraction studies.

On the basis of the X-ray diffraction results the iodine(VI) compounds obtained by the thermal decomposition of periodates can be roughly classified into three groups:

1. Compounds which do not exhibit X-ray diffraction: $Be_3I_2O_9.4H_2O$, $CaIO_4.H_2O$, $BaIO_4.H_2O$. It has not proved possible to remove the "amorphous to X-rays" nature of these compounds and to being about crystallisation even by prolonged heating at the temperature of their formation.

2. Compounds which exhibit X-ray diffraction analogous to that of the corresponding iodates: Na_2IO_4 and Li_2IO_4 behave analogously to $NaIO_3$ and $LiIO_3$ respectively. These substances are probably also amorphous in the X-ray diffraction sense but under the action of atmospheric moisture they partly decompose into iodate and periodate.

3. Compounds which exhibit a small number of weak lines which are distinguished from the lines of periodates and iodates of the corresponding metal: $MgIO_4.0.5H_2O$, $PbIO_4$, $Al_2(I_2O_7)_3$, $CdIO_4$. Probably the crystal lattice of these compounds is incompletely constructed.

Only the product of the thermal decomposition of silver orthoperiodate and mesoperiodate ($Ag_2H_3IO_6$ and Ag_2HIO_5) of composition Ag_2IO_4 shows X-ray diffraction patterns in which lines coincide with those of the Ag_3IO_5–$AgIO_3$ mixture. Clearly, therefore, the product mentioned is a mixture of mesoperiodate and iodate and cannot be considered chemically distinct[268].

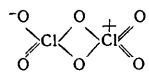
Iodine(VI) compounds are paramagnetic, unlike those of iodates and periodates which are diamagnetic. It has been found that their paramagnetism is not due to impurities but is a property of iodine(VI) compounds. Table 9 gives the values of the mass magnetic susceptibilities of these compounds and the corresponding magnetic moments (calculated from these values).

9. ANALOGUES OF THE COMPOUNDS OF IODINE(VI)

Analogues of the known compounds of iodine(VI) can be found with the lighter homologues of iodine (chlorine and bromine), with its neighbour tellurium, and also its lighter homologue selenium.

As regards chlorine(VI) and bromine(VI), compounds analogous to the iodine (VI) salts of type $M^I_2IO_4$ have not been observed but the oxides Cl_2O_6 (or ClO_3) and Br_2O_6 analogous to the oxide IO_3 are known. These oxides are unstable compounds which are formed as a result of reaction of the corresponding halogen with oxygen or ozone under the action of an electrical discharge[276,277]. An oxide of chlorine(VI) is also formed by the reaction of ozone with the oxide ClO_2 at liquid air temperature[278] or as an intermediate product in the thermal decomposition of perchloric acid[279] and of chlorine(VII) oxide at reduced pressure in the range 100–120°C. It is known[280] also that it is formed as an intermediate product in the reaction of fluorine with potassium iodate at 40–60°C. Chlorine(VI) oxide is a red, oily liquid at ordinary temperature and bromine(VI) oxide a colourless solid.

The presence of a valency of six was demonstrated[281-284] only for chlorine(VI) oxide in the gaseous state: this compound is paramagnetic and consists of ClO_3 molecules. In the liquid state this oxide dimerises. From the Raman spectra the structure of the Cl_2O_6 molecule is analogous to that of the aluminium chloride molecule:



This oxide reacts with water to form chloric and perchloric acids. Therefore some authors suggest[286-288] that it is a compound with the character of a salt $ClO_2^+ClO_4^-$.

For the oxide of bromine(VI) there has been no direct proof of a valency of six for the bromine and there has been no observation of the existence of dimeric molecules Br_2O_6 because of the instability of this compound. Dimerisation can usually be judged only by analogy with the chlorine oxide. However, results were obtained[289,290] which made it possible to rule out the older idea that this oxide is Br_3O_8. With water it gives a solution in which the presence of bromine(V) has been demonstrated. This can be explained by the following reactions:

$$Br_2O_6 + H_2O = HBrO_3 + HBrO_4 ,$$
$$2HBrO_4 = 2HBrO_3 + O_2 .$$

An analogy with the compounds of iodine of higher valency also appears in tellurium compounds. The clearest is the chemical and structural analogy of the compounds of iodine(VII) and tellurium(VI), especially for orthoperiodic and orthotelluric acids. As already noted[183] from the Raman spectra, telluric acid must be considered to be the ortho-acid H_6TeO_6 with an octahedral structure for the anion, as also happens for the periodate anion IO_6^{5-}. The infrared spectra of the two acids are also similar[184,291]. The two acids also form salts analogous in composition—for example, Na_5IO_6, and Na_6TeO_6; or Ag_5IO_6 and Ag_6TeO_6; or $Hg_5(IO_6)_2$ and Hg_3TeO_6, etc.—and in their physical properties (for example, from the solubility of the alkali metal salts). The iodine and tellurium compounds also show an ability to form heteropolyacids of analogous composition (characterised by a ratio of iodine or tellurium to metal atom of 1 : 6), for example, the acids $H_5[I(MoO_4)_6]$, $H_5[I(WO_4)_6]$, and $H_6[Te(MoO_4)_6]$ and $H_6[Te(WO_4)_6]$ respectively.

Analogous composition and properties are shown by certain complexes in which the central metal atom has an unusual valency. A series of salts of diperiodatocopper and diperiodatosilver and respectively ditelluratocopper and ditelluratosilver acids and also periodato- and tellurato-complexes of Co^{III}, Mn^{IV}, Ni^{IV}, Au^{III}, Pd^{IV}, Pt^{IV} has been described[214,217,219,220,224-228,247,253,254,292-295].

In the thermal decomposition of selenium(VI) and tellurium(VI) oxides, telluric acid, and certain tellurates, compounds of selenium(V) and tellurium(V) are formed: Se_2O_5, Te_2O_5, and also the corresponding salts. The tellurium(V) compounds are paramagnetic, like those of iodine(VI).

They are distinguished by this from the diamagnetic tellurates or telluric acid itself. The magnetic properties of the oxide Se_2O_5 have not been measured[296,297].

Siebert has recently published a paper[298] on the chemistry of the periodates.

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γ-Formyl Acids

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CONTENTS

I. Introduction 254
II. Methods of preparing γ-formyl acids 254
1. Aromatic and heterocyclic γ-formyl acids 254
2. β-Formylpropionic acids 255
3. β-Formylacrylic and β-formylcrotonic acids 256
III. Reactions of γ-formyl acids 256
IV. Investigation of the structure of γ-formyl acids by physical methods 259
V. Alicyclic γ-formyl acids 260

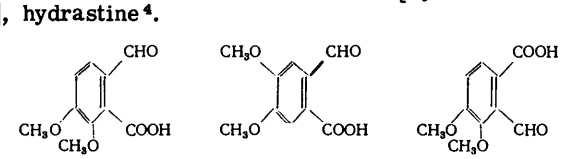
I. INTRODUCTION

The chemistry of γ-formyl acids and especially the problem of their structure has occupied the minds of many eminent investigators for over a century. It is sufficient to mention that Liebig and Wöhler, Gabriel and Libermann, Hans Meyer and Wilslicenus, Alder and Grove worked fruitfully in this field. The Soviet scientists V. M. Rodionov and M. M. Shemyakin also made a significant contribution to the study of the γ -formyl acids. Nevertheless the overwhelming majority of the studies completed up to the present time have been devoted to only an extremely limited number of γ-formyl acids, since the number of known representatives of this class of compound is generally small. They include principally the opianic and 2-formylbenzoic acids and their derivatives, halogenomucic acids, and β-formylpropionic and β-formylacrylic acids. We therefore did not set ourselves the aim of compiling an exhaustive review of all the investigations related to this problem, but have used from them only that part which, in our opinion, allows the contemporary state of the problem to be given with sufficient completeness.

II. METHODS OF PREPARING γ-FORMYL ACIDS

1. Aromatic and Heterocyclic γ-Formyl Acids

The first representative of the class of γ-formyl acids —opianic acid (I) was obtained as long ago as 1842 by Liebig and Wöhler[1-3] in oxidising one of the opium alkaloids—narcotine. Opianic acid (I) is also formed in the oxidation of the alkaloid of Canadian golden seal [*Hydrastis canadensis*], hydrastine[4].



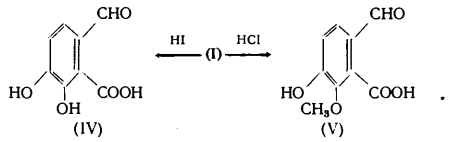
(I) (II) (III)

The structure of opianic acid was established by the work of Matthiessen and his coworkers (for example, see Ref. 5).

As well as opianic acid, γ-formyl acids isomeric with it are known: metaopianic (II)[6-8], which is formed in the

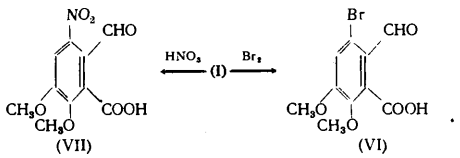
oxidation of the alkaloid cryptopine, and pseudo-opianic acid (III)[9], liberated in the oxidation of berberine.

Noropianic acid (IV)[11] is obtained in the demethylation of opianic acid by hydrogen iodide[10], whereas when hydrochloric acid is used for this purpose a partial demethylation product is formed—methylnoropianic acid (V)[12,13]:



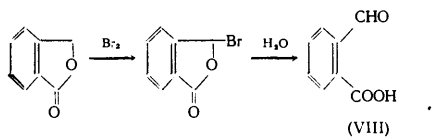
(IV) (V)

Of the derivatives of opianic acid, mention must be made of those obtained from it by the action of bromine or by nitration, the well-known 3-bromo-opianic (VI)[14-16] and 3-nitro-opianic (VII)[14,17,18] acids, and also the reduction products of the latter: 3-nitroso- and 3-amino-opianic acids[19]:



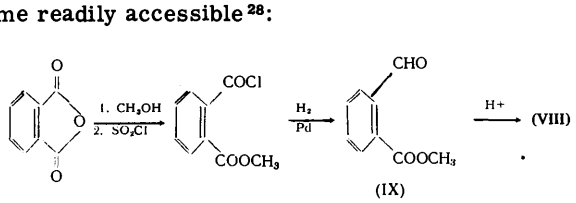
(VII) (VI)

In their chemical and physical properties 2-formylbenzoic acids are very similar to opianic acid. The first method of obtaining 2-formylbenzoic acid itself (VIII), developed in 1886 by Racine[20-22], consists in the bromination of phthalide to bromophthalide and subsequent careful hydrolysis:



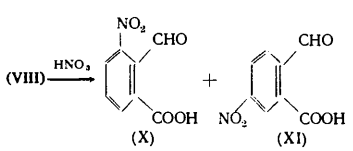
(VIII)

Another method of making 2-formylbenzoic acid which has been well studied is the oxidation of naphthalene with ozone[23,24] or potassium permanganate[25,26]. The best method of making this formyl acid is based on the Rosenmund reaction (yield reaches 60%, calculated on phthalic anhydride)[27]; in this way the normal methyl ester (IX) became readily accessible[28]:



(IX)

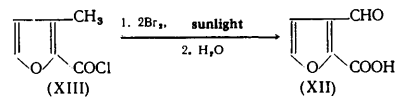
In the direct nitration[29,30] of 2-formylbenzoic acid a mixture of 3- and 5-nitro-2-formylbenzoic acids (X) and (XI) is formed, with the latter preponderating:



(X) (XI)

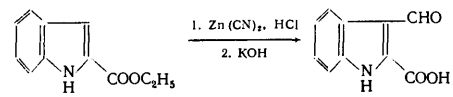
Several substituted 2-formylbenzoic acids were synthesised by Chakravarti and coworkers[31-34].

Several representatives of heterocyclic γ-formyl acids have been described. The first of these chronologically was probably 3-formylfuran-2-carboxylic acid (XII) obtained in 1924 by Japanese investigators[35] on brominating (with subsequent hydrolysis) elsholtzia acid chloride (XIII):



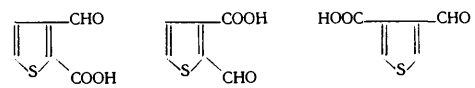
(XIII) (XII)

3-Formylindole-2-carboxylic acid (XIV)[36-38] can serve as an example of a γ-formyl acid of a nitrogen heterocycle:



(XIV)

In 1963 the Swiss scientist Gronowitz and his coworkers[39,40] synthesised three γ-formyl acids of the thiophen series:



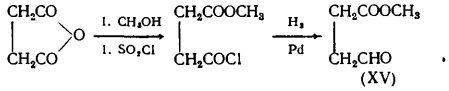
2. β-Formylpropionic Acids

The various β-formylpropionic or formylsuccinic acids which serve as the initial compounds for the synthesis of derivatives of the natural growth substance heteroauxin (β-indolylacetic acid)[41-46] are extremely interesting. In several instances these substances also exhibit antibiotic properties.

The first representatives of this class of compound, β-formylpropionic and β-formyl-α-methylpropionic acids were obtained in 1899 by Perkin Jnr. and Sprankling[47], by the condensation of sodiomalonic ester and, respectively, sodiomethylmalonic ester with bromoacetaldehyde acetal with subsequent hydrolysis and decarboxylation. Later[48,49] a large number of alkyl-substituted β-formylpropionic acids was synthesised by this method. β-Formyl-α-methylpropionic acid was also obtained from ketomethylglutaric acid[50].

Wilslicenus and coworkers[51] effected the synthesis of β-formylpropionic acid by starting from formylsuccinic acid, which they subjected to hydrolysis by heating with water in a sealed ampoule at 120–130°C. The hydrolysis of formylsuccinic ester by an aqueous solution of oxalic acid has also been described[52,53]. β-Formyl-α-phenylpropionic acid was synthesised in a similar manner[54].

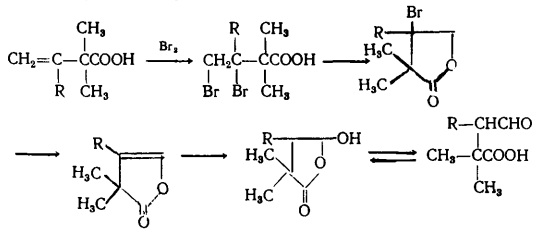
Johnson and coworkers[55] proposed a good method for the synthesis of methyl β-formylpropionate (XV) with the aid of the Rosenmund reaction:



(XV)

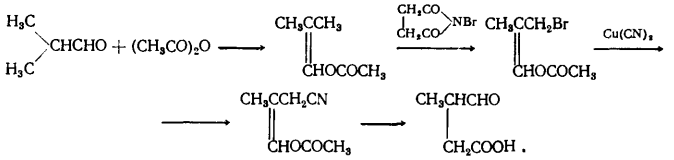
Application of the Rosenmund reaction to monoesters of various dicarboxylic acids is evidently a promising path to a variety of γ-formyl acids and also to γ-formyl acids of another structure.

Blaise and Kourtot[56,57] obtained trisubstituted β-formylpropionic acids from the corresponding trisubstituted βγ-unsaturated acids:

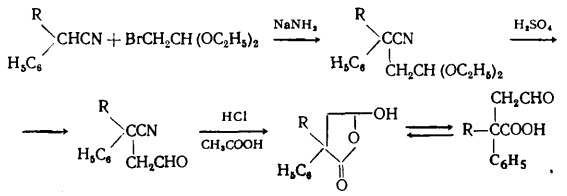


where R = CH_3, C_6H_5.

A new synthesis of β-formylbutyric acid was recently[58] effected according to the following scheme:

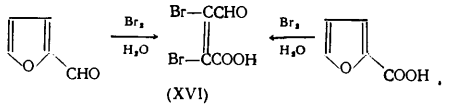


In 1963 Salmon-Legagneur and Paulain[59,60] developed a general method for the preparation of αα-disubstituted β-formylpropionic acids based on the condensation of the nitriles of alkyl aryl carboxylic acids with bromoacetaldehyde acetal in the presence of sodium amide, followed by hydrolysis:



3. β-Formylacrylic and β-Formylcrotonic Acids

Of this type of γ-formyl acid, the halogenomucic and dihalogeno-β-formylacrylic acids have long been known and have been well investigated. These compounds are usually obtained by starting from furan derivatives. For example, in the vigorous bromination of furfural or pyromucic acid in aqueous solutions bromomucic acid (XVI) is obtained in excellent yield[61-63]:



(XVI)

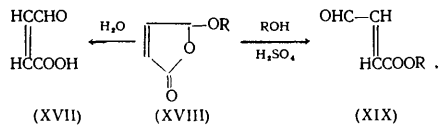
Chloromucic acid was synthesised in an analogous manner[61].

The halogen atoms and the double bond in the halogenomucic acids are distinguished by extremely low reactivity, because of which these compounds have not been used for the synthesis of new representatives of γ-formyl acids to any significant extent. Only the products of the replacement of the bromine atom at the α-carbon atom of bromomucic acid by hydroxy-, phenoxy-, and arylaminogroups[64-66] and also the replacement of the chlorine atom of chloromucic acid by the hydroxyl group[64] are known.

Of great interest for synthetic organic chemistry are the β-formylacrylic and β-formylcrotonic acids which do not contain halogen atoms; they were, for example, used for the synthesis of carotenoids by the Wittig reaction[67].

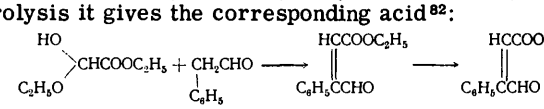
The use of ψ-esters of β-formylacrylic acid as dienophiles in the diene condensation allowed a series of representatives of a previously unknown class of alicyclic γ-formyl acids to be obtained[68-74].

The methods described earlier for obtaining *cis*-β-formylacrylic acid (XVII) were based on the oxidation of pyromucic acid[75,76] or furfural[77] by various oxidants. Later Shenk[78-80] developed a convenient method for obtaining the ψ-esters of *cis*-β-formylacrylic acid (XVIII) by the photochemical oxidation of furan derivatives. Hydrolysis of the ψ-esters with boiling water leads to the corresponding *cis*-acid (XVII)†, whereas on boiling alcoholic solutions of the ψ-esters in the presence of catalytic amounts of sulphuric acid esters of the *trans*-isomer (XIX) are obtained:

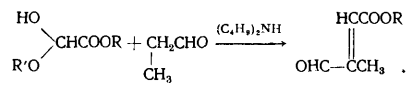


(XVII) (XVIII) (XIX)

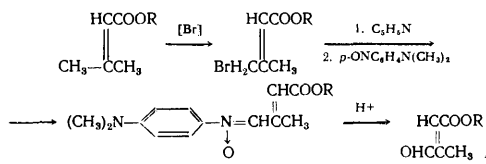
Photochemical oxidation was not used for the synthesis of substituted β-formylacrylic acids, although there are undoubted prospects for its use for such purposes. A few well-known representatives of γ-formyl acids of this type are obtained by other methods. Thus in the condensation of the hemiacetal of ethylglyoxalate with phenylacetaldehyde, ethyl β-formyl-β-phenylacrylate is formed, and on hydrolysis it gives the corresponding acid[82]:



Esters of β-formylcrotonic acids are obtained in good yields in the condensation of the hemiacetals of the esters of glyoxalic acid with crotonaldehyde in the presence of dibutylamine[67]:

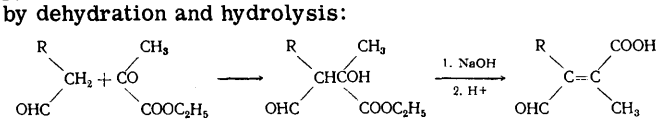


In another method[83] various esters of ββ-dimethylacrylic acid were subjected to bromination by *N*-bromosuccinimide, then the γ-bromo-β-methylcrotonic esters produced were treated (in the form of pyridinium salts) with *NN*-dimethyl-*p*-nitrosoaniline. Careful hydrolysis of the nitrones thus obtained led to the corresponding esters of β-formylcrotonic acid:



Ethyl β-formylcrotonate was also synthesised from β-methylcrotonic ester[84].

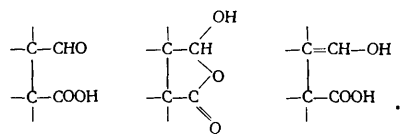
Recently Schreiber and Wermuth described[85] the production of a series of *trans*-β-formyl-β-alkyl-α-methylacrylic acids and their esters by condensation of esters of pyrotartaric acid with various aliphatic aldehydes, followed by dehydration and hydrolysis:



† *cis*-β-Formylacrylic acid is also obtained from 2-acetoxyfuran by bromination and subsequent hydrolysis[81].

III. REACTIONS OF γ-FORMYL ACIDS

The characteristic property of all the γ-formyl acids is their ability to react in two tautomeric forms[86]: the α-form (aldehydic) (XX) and the ψ-form (hydroxy-lactone) (XXI). The aliphatic and alicyclic γ-formyl-acids, although having one unsubstituted hydrogen atom at the β-carbon atom, are capable in some instances of also reacting in a third tautomeric form—enol (XXII)[86]:



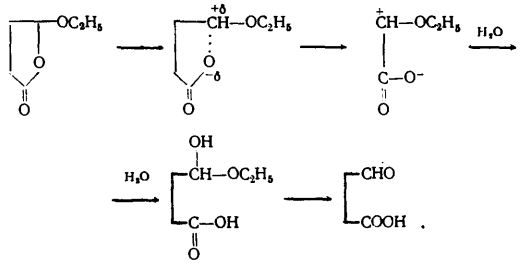
(XX) (XXI) (XXII)

Between these forms there is a mobile chemical equilibrium, therefore the establishment of the structure of γ-formyl acids in the isolated state acquires a special significance. Furthermore, it is very important to investigate the conditions under which displacement of the equilibrium to one of the tautomeric forms takes place, since such a displacement can be determined not only by the influence of the external medium but also by the structure of the γ-formyl acids.

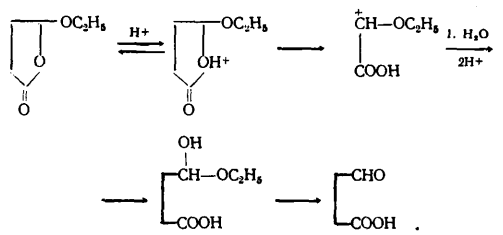
The problem of the structure of isolated γ-formyl acids was presented to chemists immediately after the discovery of the first of their representatives and more than a century later it still remains the subject of lively discussion[87,88]. In order to discriminate in this question it is necessary to first consider in detail the chemical behaviour of γ-formyl acids and to try to understand which factors determine their ability to react in any particular tautomeric form. Above all, it can be assumed as a working hypothesis that in the conditions of a medium which does not facilitate tautomeric transformations aldehydo-acids will react in that form in which they exist in the pure state and form a compound corresponding to this form. Thus it appears that crystalline γ-formyl acids are formed with astonishing ease even when alcoholic solutions of the corresponding ψ-esters, that is, ethers of the hydroxy-lactone form are kept for prolonged periods[89-91]. This conversion takes place more rapidly on heating[7,29,86,92,93] or in the presence of mineral acids[2,86,91,94-96]. A similar reaction has been described for many γ-formyl acids and is evidently a typical feature of those which are incapable of showing tautomerism in alcoholic solution. If the γ-formyl acids exist as a mixture of tautomeric forms then they would be expected to form a mixture of α- and ψ-esters in alcoholic solution. This occurs, for example, with β-formylpropionic, β-formyl-α-methylpropionic, and other α-alkyl-β-formylpropionic acids[47,50,52-58], which are liquids under ordinary conditions. The mercaptans behave like alcohols; they readily react with crystalline γ-formyl acids[97] to form compounds corresponding to their ψ-forms. For a long time examples have been known when either only the ψ-esters or their mixture with the corresponding α-esters are formed in the esterification of γ-formyl acids, depending upon the reaction conditions. Such a phenomenon was, for example, observed on heating 2-formylbenzoic acid with methanol in the presence of sulphuric acid[91]. These facts found explanation in the work of Kirpal and Zieger[98], who showed that normal formyl esters are products of the isomerisation of the ψ-esters formed initially, which takes place under the influence of the mineral acid. A similar isomerism is well known for esters of γ-keto-acids[99,100].

A characteristic property of the ψ-esters of γ-formyl acids is also the exceptional ease of their saponification: many of these are converted into the initial γ-formyl acids even on simple heating with water[29,67,69,86,88]. In the presence of acid catalysts this reaction takes place more rapidly.

On the basis of kinetic investigations of the hydrolysis of the ethyl ψ-ester of β-formylpropionic acid, Fife[101] concluded that a neutral medium is much more favourable for the hydrolysis of such bifunctional compounds of acylal-acetal structure than for ordinary acetals or esters. He proposed the following mechanism for the hydrolysis of a ψ-ester in neutral medium, which is a first-order reaction:

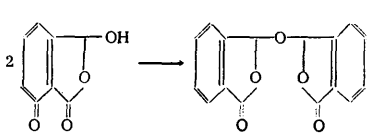


In the presence of mineral acids, in his opinion, the hydrolysis of a ψ-ester takes place by a somewhat different scheme:



On heating γ-formyl acids with acetic anhydride (in some instances in the presence of sodium acetate or sulphuric acid), acetyl derivatives of their hydroxy-lactone form are always produced[21,62,102,103]. The reaction of γ-formyl acids with phosphorus(V) chloride or thionyl chloride also leads to cyclic derivatives[104-108].

When heated above their melting point, aromatic γ-formyl acids are converted into ψ-anhydrides[21,29,103,107,109], for example:



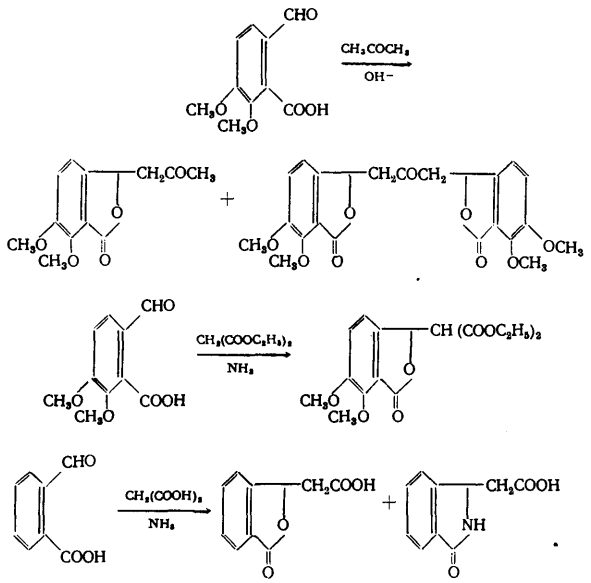
Finally, derivatives of the ψ-form are obtained by the action on γ-formyl acids of such weak bases as aromatic amines[12,110-117].

Since the α-form of the γ-formyl acids exhibits incomparably more reactive functional groups than the hydroxy-lactone form, in all those instances when the α-form arises in a reaction medium, it specifically takes part in the chemical conversion. In this, when the reaction product is insoluble (semicarbazone, and also other analogous derivatives) or is incapable of further conversion under the given conditions (for example, a methyl ester formed under the action of diazomethane), the tautomeric equilibrium is completely shifted to the side of the α-form. When the derivative of the α-form which is produced can undergo secondary transformations, for example, be cyclised into a

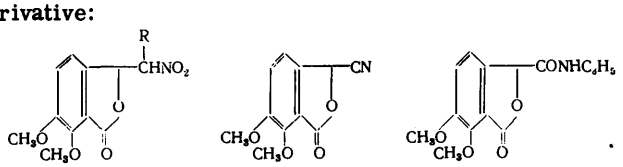
lactone, then the final reaction products are derivatives of the ψ-form of the original γ-formyl acid. Thus, most formyl acids react with Schiff's reagent in alcoholic solutions[86,117] and smoothly form crystalline derivatives with hydroxylamine, hydrazine, and substituted hydrazones[76, 111,112,118-120].

Reactions in which the pure α-form of γ-formyl acids are produced are the reactions of their neutralisation, leading to the corresponding metal salts[1,3,121]. By starting from the potassium opianate it is possible to obtain compounds corresponding to the normal form with yields of ~ 80%; for example, with benzyl chloride it gives the α-benzyl ester, and with chloroacetone, the α-acetonyl ester[121,122].

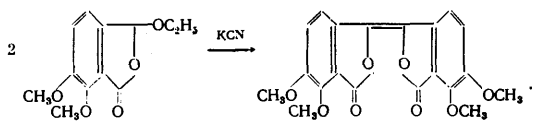
A series of conversions of the γ-formyl acids is known in which the nature of the reagents employed, the conditions of the medium, or the presence of bases would lead us to expect the formation of derivatives of the α-form but nevertheless the final products are derivatives of cyclic structure. Thus, the condensation in the presence of alkali or ammonia of opianic and certain other formyl acids with ketones[123-126], malonic ester, and malonic acid[127-129] leads to compounds corresponding to the ψ-form:



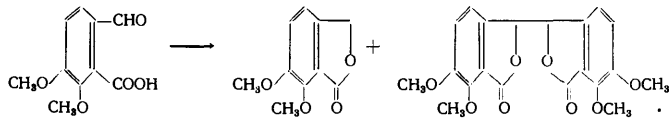
The reaction of γ-formyl acids with nitromethane and other aliphatic nitro-compounds[130-132], potassium cyanide[128,129], or phenyl isocyanide[133] also leads to a cyclic derivative:



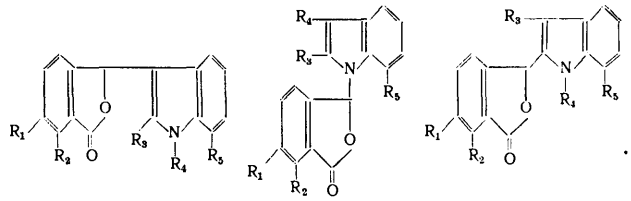
The action of anhydrous potassium cyanide on ethyl ψ-ester of opianic acid in absolute alcohol leads to the formation of meconilidenemeconine[134]:



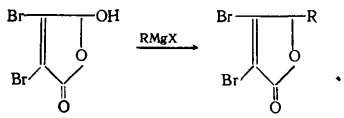
Meconin[5,6-dimethoxyphthalide (Ed. of Translation)] is obtained by the reduction of opianic acid with zinc and sulphuric acid[135] or sodium amalgam[135,136]. Electrolytic reduction of potassium opianate in an apparatus without a diaphragm but with a mercury cathode[136-138] leads to a mixture of meconine and other stereoisomeric dimeconyls (racemic and meso):



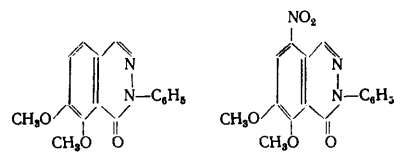
In the condensation of aromatic γ-formyl acids with indole and its derivatives[139-142], various meconylindoles are obtained, the structure of which depends on the position of the substituents in the pyrrole ring:



This reaction was later[142] studied also for chloromucic acid and also extended to other heterocyclic systems: substituted pyrroles, carbazole, indazole, and benzotriazole. For 2-formylbenzoic acid a reaction mechanism was established[141,142] which included the intramolecular catalytic activation of the aldehyde groups by the carboxyl group. The reaction of γ-formyl acids with alkyl (or aryl) magnesium halides leads to compounds which contain a γ-lactone grouping[143-147], for example:



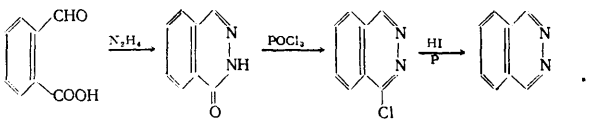
Finally, many reactions of γ-formyl acids are known in which the interaction takes place simultaneously at the aldehyde and carboxyl groups. γ-Formyl acids react in this way with various nitrogen compounds (aromatic o-diamines, hydrazine, substituted hydrazines), leading to derivatives of pyridazine, phthalazine, isocarbostyril, and other heterocyclic systems. Thus as long ago as 1886, in an attempt to obtain phenylhydrazones from opianic and nitro-opianic acids, Liebermann[148] unexpectedly isolated the products of the removal of two water molecules from them. To these compounds, named opiazone (XXIII) and nitro-opiazone (XXIV), Liebermann ascribed the structure of heterocyclic derivatives with two adjacent nitrogen atoms, this being based on the work of Roser[149] who obtained analogous products by the condensation of phenylhydrazine with o-carboxybenzoylacetic acid and related acids:



(XXIII) (XXIV)

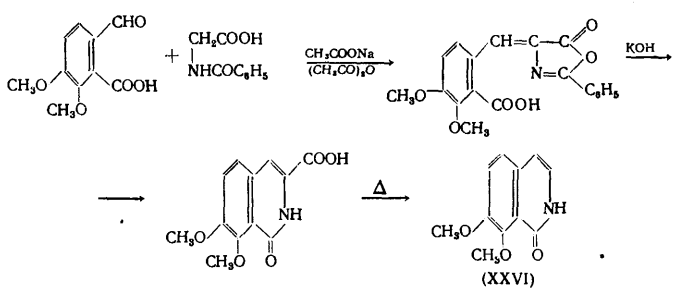
Later the same reaction was studied by the examples of 2-formylbenzoic[21,150], bromo-opianic[119], and bromomucic[151] acids and in every instance analogously constructed heterocyclic compounds were formed.

In 1897 Gabriel and Eschenbach[152] studied the condensation of phthalaldehydric acid with hydrazine itself and developed a method of reduction of the keto-groups formed therein, which preceding workers could not do. In this way a general method of synthesis of the derivatives of a new heterocyclic system, which Liebermann[148] named phthalazine (XXV), was discovered:



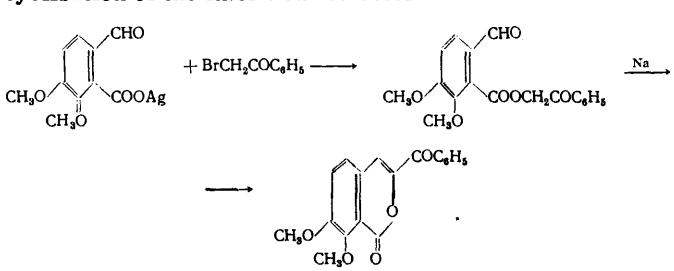
(XXV)

In their classical investigations of the alkaloids of the berberine group, Perkin, Jnr. and his coworkers[153] cleverly used the condensation of opianic acid with hippuric acid to synthesise the 7,8-dimethoxyisocarbostyril (XXVI) which they needed:

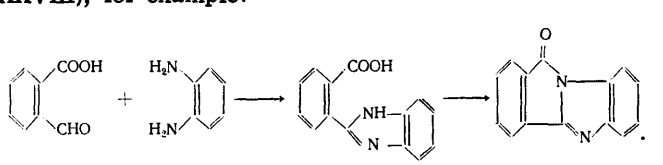


(XXVI)

In an analogous way[153] isocarbostyril itself was obtained from phthalaldehydic acid. 3-Benzoyl-7,8-dimethoxyisocoumarin was synthesised[153] by the reaction of silver opianate with ω-bromoacetophenone and the subsequent cyclisation of the intermediate ester:



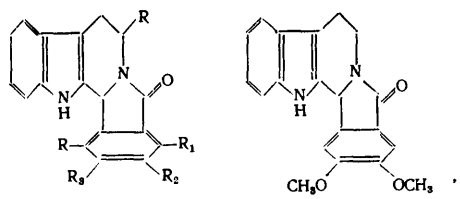
Complex polycyclic nitrogen-containing compounds of alkaloid type can also be obtained on the basis of γ-formyl acids. Even as long ago as the eighteen-nineties Bistrzycki[154,155] showed that 2-formylbenzoic and opianic acids react in the cold with *o*-phenylenediamine and *o*-toluylenediamine, forming cyclic amidines (XXVII), which on boiling with acetic anhydride give the corresponding amidones (XXVIII), for example:



(XXVII) (XXVIII)

Later, Stephenson[156,157] described products of the condensation of phthalaldehydric acid also with other aromatic diamines: with ωω'-diamino-*o*-xylene. 2,2'-diaminobiphenyl, 1,8-diaminonaphthalene, and *o*-aminobenzylamine.

Recently[158], with the aim of synthesising new hypertensive preparations, analogues of reserpine, condensations were effected with the aid of the Pictet–Spengler reaction between 2-formylbenzoic, opianic, metaopianic, and 3,4,5-trimethoxyphthalaldehydric acids and tryptophan and tryptamine. Among the series of pentacyclic compounds thus obtained which contain the β-carboline nucleus, weakly hypertensive activity appeared only in the derivative of metaopianic acid (XXIX):



(XXIX)

IV. INVESTIGATION OF THE STRUCTURE OF γ-FORMYL ACIDS BY PHYSICAL METHODS

Hence, as is evident from the preceding chapters, the study of the chemical behaviour of γ-formyl acids did not provide a conclusive solution for the perennial controversy about their structure‡. A revolutionary role in this sense was played by spectroscopy, the credit for the first use of which for solving the complicated problem of the structure of the γ-formyl acids belongs to Buu-Hoi and his coworkers[163–165]. In 1939–1941 they studied the ultraviolet spectra of 2-formylbenzoic, opianic, 6-bromo-opianic, 6-nitro-opianic acids. It was shown that all these γ-formyl acids in the crystalline state and in chloroform solutions exist in the hydroxy-lactone form. In aqueous solution 2-formylbenzoic and opianic acids have an acyclic form, whereas 6-bromo- and 6-nitro-opianic acids in alcoholic and aqueous–alcoholic solutions exist as equilibrium mixtures of both tautomeric forms. The last two acids, which contain substituents in the *ortho*-position to the aldehydic group, seemed capable of existing in the acyclic form only in strongly alkaline aqueous solutions.

After the ultraviolet spectra, infrared spectra were also used successfully for studying ring–chain tautomerism of γ-formyl acids. Thus with the aid of infrared spectra it was shown that 2-formylbenzoic acid is in a cyclic form in the crystalline state[166]. The extremely thorough work of Wheller and coworkers[167] appeared later. These authors synthesised over fifty derivatives of 2-formylbenzoic acid, the study of the infrared spectra of which in liquid paraffin showed that they exist solely in cyclic form. The absorption spectra of a series of other γ-formyl acids, studied in recent years, also show that these compounds are found exclusively in the cyclic form in the crystalline state, but in solutions they are in the form of equilibrium mixtures of both tautomeric forms, and the position of the equilibrium depends on the dielectric constant of the solvent, its pH, and many other external factors[58,168–174].

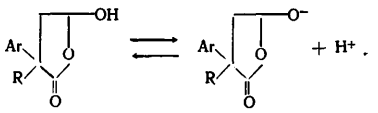
On the other hand, thiophen analogues of 2-formylbenzoic acid (see p. 255) have been shown by Gronowitz and

‡ It must be emphasised that a correct solution of this problem is important not only for the theoretical organic chemistry alone; it also has biological importance, since keto-lactol tautomerism evidently determines the physiological activity of certain antibiotics[159–162].

coworkers[39,40]—on the basis of the NMR spectra in chloroform, dioxan, acetone, and water and also with the aid of ultraviolet and infrared spectra—to exist solely in the acyclic form and it was even found that on esterification in the presence of sulphuric acid 3-formylthiophen-2-carboxylic acid gives a normal ester. The reasons for such a phenomenon are evidently purely geometrical: the incapability of formyl acids of the thiophen series to form lactol tautomers is probably due to differences in the C–C distances and in the values of the valence angles in the benzene and thiophen molecules.

Study of the structure of halogenomucic acids with the aid of NMR showed that they were completely free from an acyclic form, but in the presence of an equivalent quantity of potassium hydroxide halogenomucic acids are converted completely into the acyclic form[170]. According to the ultraviolet and infrared spectra, *cis*-β-formylacrylic acid also has the lactol structure[175].

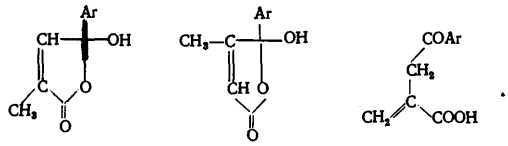
It is interesting to note that for certain substituted β-formylpropionic acids the cyclic form is so stable that it even exhibits a slight acidity, owing to the weak dissociation of the hydrogen of the lactol hydroxyl. These properties are exhibited by αα-disubstituted β-formylpropionic acids which contain not less than one aromatic substituent[176]:



It is necessary to mention here, though briefly, the information about the structure of the nearest relatives of the γ-formyl acids, among which belong above all the γ-keto-acids, with chemical properties very reminiscent of them. The structure of the γ-keto-acids has been extensively studied by spectroscopic methods. Various *o*-benzoylbenzoic acids have been investigated in considerable detail in this respect[177–181]. It was found that most of the methyl-substituted *o*-benzoylbenzoic acids studied exist in the crystalline state and in chloroform or carbon tetrachloride solutions as acyclic tautomers[177–180]. Only acids with a methyl group in the *ortho*-position to carboxyl are an exception, especially 2-benzoyl-3,6-dimethylbenzoic acid, which even in methanol contains only 7% of the keto-acid form[179]. Functional derivatives of *o*-benzoylbenzoic acid (containing halogens, CN, NO_2, and other groups), also have, according to the infrared spectra, an acyclic structure (18 compounds were studied) in the solid state, but form equilibrium mixtures in solutions, with the predominance of the tautomer with an open chain[180]. A well-expressed linear relationship between the free energy and Hammett constant (σ) of the substituents is observed for these compounds.

o-Acetylbenzoic acids have predominantly cyclic structure[178,180]. The increased stability of the tautomers with an open chain in the example of *o*-benzoylbenzoic acid may be connected with the gain in energy due to the formation of a conjugated system.

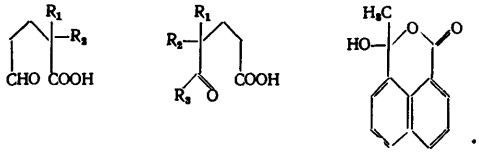
Lutz and coworkers[182] showed with the aid of ultraviolet spectra that various *cis*-β-aroyl-α-methyl- and *cis*-β-aroyl-β-methyl-acrylic acids (XXX) and (XXXI) in alcoholic solutions exist predominantly in the lactol form§. On the other hand, saturated analogues of these compounds—β-aroylbutyric acids, and also β-aroyl-α-methyleneacrylic acids (XXXII) have an open structure:



(XXX) (XXXI) (XXXII)

The structure of the β-acylacrylic acids is closely connected with their stereochemistry. Thus, on the basis of spectroscopic data it was found that β-acetylacrylic acid, with the *trans*-configuration, and also the *trans*-isomer of β-pivaloylacrylic acid are true keto-acids, whereas *cis*-β-acetyl-α-methylacrylic and *cis*-β-pivaloylacrylic acids are lactols[175,184,185]. The solution of the problem of the configuration of the stereoisomeric β-pivaloylacrylic acids on the basis of an examination of their tautomeric structure with the aid of NMR spectra[184] is probably the first example of the use of spectra for such a purpose¶.

Aliphatic mono- and di-substituted δ-formyl acids (XXXIII), recently synthesised by Salmon-Legagneur and coworkers[186,187], are, according to their infrared spectra, tautomers with an open chain. The aliphatic δ-keto-acids (XXXIV) also have an analogous structure[188–190]:

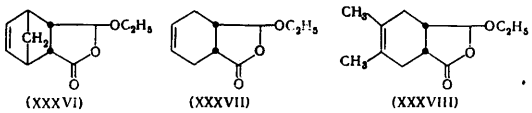


(XXXIII) (XXXIV) (XXXV)

However, 8-acetyl-1-naphthoic acid (XXXV) exists only in the lactol form[191].

V. ALICYCLIC γ-FORMYL ACIDS

γ-Formyl-acids of the cycloaliphatic series remained unknown until very recently, becoming accessible only in 1958, thanks to the work of Alder and Fariña[68], who found that the ethyl ψ-ester of β-formylacrylic acid (XVIII) is capable of undergoing a diene condensation with cyclopentadiene, bivinyl, and 2,3-dimethylbutadiene, forming the corresponding adducts (XXXVI)–(XXXVIII)†:

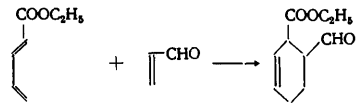


(XXXVI) (XXXVII) (XXXVIII)

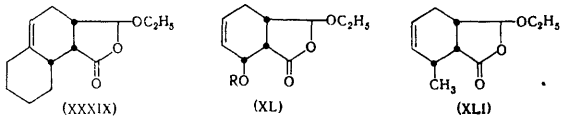
§ For *cis*-β-(4-bromophenyl)-β-methylacrylic acid this was established even earlier by polarograph[183].

¶ See p.262 for the analogous use of infrared spectroscopy in several alicyclic-formyl acids.

† In 1965 the synthesis of an α-ester of an alicyclic γ-formyl acid effected by another path was described[192]:



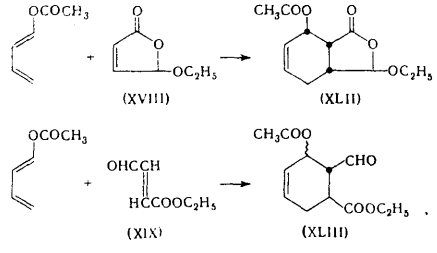
It was found later that an analogous condensation also takes place with 1-vinylcyclohex-1-ene[72], 1-acetoxybutadiene[69], and *trans*-piperylene[74], leading to the adducts (XXXIX)–(XLI):



(XXXIX) (XL) (XLI)

Furan and dienes, like styrene, do not react with the ψ-ester (XVIII)[68]. Instead of the ψ-ester of β-formylacrylic acid the corresponding *cis*-acid (XVII) and also the normal ethyl ester of its *trans*-isomer (XIX) can be used in the diene synthesis[68,69]. The adducts of the diene synthesis obtained with the ψ-ester (XVIII), are readily converted into the corresponding acids or normal esters, which contain a free formyl group and are capable of entering into the Knoevenagel reaction[68,69,73].

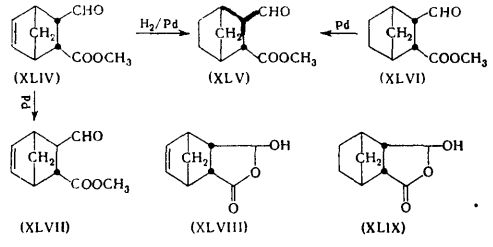
In studying the diene condensation of 1-acetoxybutadiene with the ethyl ψ-ester of β-formylacrylic acid and also 1-acetoxy and 1-methoxy-butadiene with the ethyl α-ester of *trans*-β-formylacrylic acid, Farina and coworkers[69] observed an interesting fact. It appeared that the adducts (XLII) and (XLIII) obtained from the *cis*- and *trans*-dienophiles have not only different configuration but also different structure, which is evidently due to the different orientation abilities in the diene synthesis of the functional groups of the dienophiles:



(XVIII) (XLII)

(XIX) (XLIII)

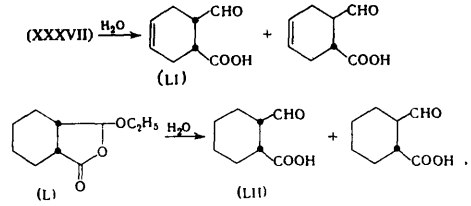
The synthesis and stereochemical conversions of the adducts of the diene condensation of the ethyl ψ-ester of β-formylacrylic acid (XVIII) with cyclopentadiene, 2,3-dimethylbutadiene, and bivinyl were subsequently subjected to a more detailed study[70,71]. Here in particular it was found that the hydrogenation of the unsaturated *cis*-γ-formyl ester (XLIV) is accompanied by the simultaneous isomerisation, leading to the saturated *trans*-γ-formyl ester (XLV), which is obtained also in the simple shaking of the saturated *cis*-formyl ester (XLVI) with reduced palladium catalyst. The unsaturated *cis*-γ-formyl ester (XLIV) is isomerised in an analogous manner, giving the *trans*-isomer (XLVII). Such astonishingly easy isomerisation of the α-esters (XLIV) and (XLVI) and the incapability to isomerisation under the same conditions of the corresponding γ-formyl acids (XLVIII) and (XLIX) are chemical proofs of the lactol structure of the latter[70]:



(XLIV) (XLV) (XLVI)

(XLVII) (XLVIII) (XLIX)

In contrast to Alder and Farina's results[68], it was shown that saponification of the adduct (XXXVII)[71] with boiling water and also saponification of its hydrogenation product (L) (contrary to the behaviour of the analogous derivatives obtained from cyclopentadiene[70]) is accompanied by isomerisation and leads to mixtures of *cis*- and *trans*-γ-formyl acids:



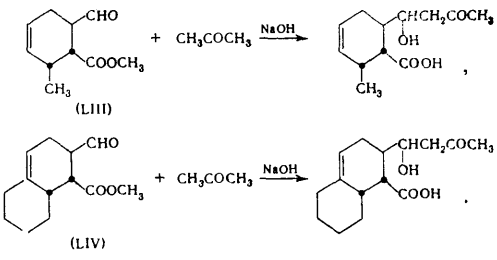
(LI)

(L) (LII)

On this basis it can be suggested that the γ-formyl acids (LI) and (LII) exist in aqueous solution as mixtures of tautomeric forms.

The γ-formyl acids and their derivatives obtainable with the aid of the diene condensation of the ethyl ψ-ester of β-formylacrylic acid (XVIII) with piperylene[74] and 1-vinylcyclohexene are distinguished by a considerable tendency to epimerisation[72,193]. Diene reactions in which these unsymmetrical dienes participate proceed with structural and spatial selectivity, leading mainly to the adducts mentioned above (XXXIX) and (XLI). Hydrolysis of the latter even in neutral conditions is accompanied by partial isomerisation and the *cis*-γ-formyl acids which are formed contain the *trans*-isomers as impurity. Therefore the preparation of the pure γ-formyl acids and their derivatives by these means is practically unattainable. The especially ready isomerisation is observed in the bicyclic series[193]. The catalytic hydrogenation of adducts (XXXIX) and (XLI) takes place readily and in the case of adduct (XXXIX) is stereo-directed—to the side opposite the lactol ring. From the saturated ψ-esters obtained in this manner the corresponding *cis*- and *trans*-formyl acids have been synthesised; these, and also their normal esters, are distinguished by a somewhat smaller tendency to *cis*–*trans*-isomerism than their Δ^4-unsaturated analogues.

The esters of the alicyclic γ-formyl acids of the cyclohex-4-ene series are characterised by considerable inertness in nucleophilic additions at the aldehyde group. Thus, the *cis*-*trans*-formyl ester (LIII) is only saponified, and does not form an acetylenic alcohol under the action of sodium acetylide in liquid ammonia‡[74]. The condensation of the *cis*-*trans*-γ-aldehydo-esters (LIII) and (LIV) with acetone under the influence of dilute sodium hydroxide§ takes place to only 10–15% extent[74,193].



(LIII)

(LIV)

Such behaviour of the formyl group was explained by its participation in an intramolecular interaction with the π-electrons of the double bond (supra-annular effect)[194,195],

‡ The corresponding *cis-cis*-formyl ester in this is isomerised into the *trans*-isomer.

§ Hydrolysis of the ester group takes place simultaneously.

which is confirmed also by diminished reactivity of the double bond in such compounds as was shown by determination of the thiocyanate numbers[74,193].

Interesting regularities were observed in studying the infrared spectra of γ-formyl acids[74,193], derivatives of the adducts of the ψ-esters (XVIII) with 1-vinylcyclohexene and *trans*-piperylene (XXXIX) and (XLI). It was found that unsaturated γ-formyl acids of both the *cis*- and *trans*-series exist in carbon tetrachloride solution as equilibrium mixtures of almost equal amounts of the two tautomeric forms. On the other hand, the corresponding unsaturated γ-formyl acids of *cis*-configuration have under these conditions the structure of lactols, whereas the *trans*-acids are true γ-formyl acids. Evidently infrared spectroscopy is a rapid and reliable method of demonstrating the configuration of stereoisomeric alicyclic γ-formyl acids (especially in the presence of pairs of isomers[85,168].

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Progress in the Chemistry of the 1,3-Dioxans

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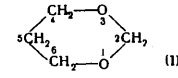
CONTENTS

I. Introduction 264
II. Methods of synthesis of 1,3-dioxans 265
III. Stereochemistry of 1,3-dioxans 267
IV. Chemical changes of the 1,3-dioxans 270
V. Use of the 1,3-dioxans 273

I. INTRODUCTION

In recent years there has been a considerable increase in interest in the 1,3-dioxans. There has been a review of the chemistry of these compounds[1] but it is incomplete and contains references to the literature only up to 1955. The present review fills some of the gaps in this earlier review and surveys the literature for 1955–1965. Furthermore, the present article examines the problem of the stereochemistry of the 1,3-dioxans, which was not considered systematically earlier. In this the authors consider it necessary to express their viewpoint on some of the complicated stereochemical problems relating to works they have carried out.

The first information on 1,3-dioxans appeared in 1865, however, the simplest of them, 1,3-dioxan itself[1], was synthesised only in 1902.[2] Compounds of this type were named 1,3-dioxans (or *meta*-dioxans) only by the external similarity in structure to 1,4-dioxans. However, the latter are simple ethers, whereas 1,3-dioxans are cyclic acetals (ketals).


(I)

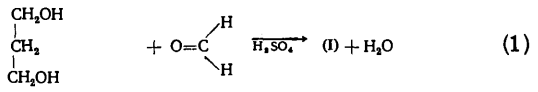
There is no great industrial production of most 1,3-dioxans. However, there are now great possibilities for their rational use. Many substituted derivatives of (I) were found to be good solvents. Some of the compounds of this type are physiologically active and have found application as effective spasmolytic and antihistamine preparations, depressants of the central nervous system, and even antibiotics. A series of 1,3-dioxans seemed an important intermediate product in organic synthesis, particularly in the synthesis of isoprene and other conjugated dienes.

II. METHODS OF SYNTHESIS OF 1,3-DIOXANS

All the preparative methods of synthesis of 1,3-dioxans can be classified in the following main groups.

1. Production of 1,3-Dioxans by the Reaction of Aldehydes and Ketones with Polyhydroxy-Compounds

This method was first proposed by Henry[2] for the synthesis of (I) by the scheme (1):

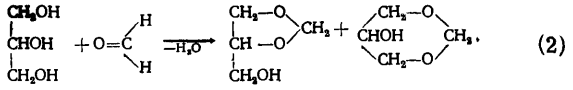


(1)

and was then improved by many authors. Various 1,3-diols and aldehydes were used in the reaction. In addition to sulphuric acid, which several authors have used as catalyst[3-8], other condensing agents have been proposed: hydrochloric acid[9-12], phosphoric acid[13-17], *p*-toluenesulphonic acid[18-26], and ion-exchange resins[27-31]. The use of *p*-toluenesulphonic acid gives good results; when it is employed the resinification and formation of side-products which complicates the condensation catalysed by mineral acids, are not observed. The use of sulphonic cation-exchange resins has still not been extensively studied but there are results which suggest that these are evidently the best catalysts for the reaction considered. In practice, the cation-exchange resins can be used repeatedly, and moreover their use greatly simplifies the purification of the dioxans being synthesised.

An important improvement in the original method of making 1,3-dioxans by the above process was the use of azeotropic distillation of the water formed during the reaction[18,32], which prevented the back reaction of hydrolysis of the dioxans and had special value for obtaining ketals of the type being considered. Besides, in addition to this technique, variations in the method under consideration have been used in which the condensation is effected in an aqueous medium[33].

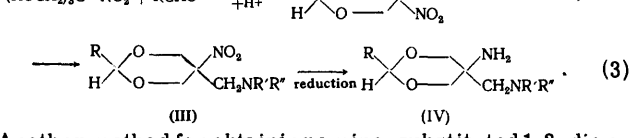
The condensation of polyhydroxy-compounds with aldehydes takes place especially well. The structure of the aldehydes has little influence on the course of the reaction. With ketones the reaction is much more difficult, owing to the greater difficulty in obtaining ketals for stereochemical reasons. It was only in 1938 that Böeseken succeeded in condensing a series of aliphatic, alicyclic, and aromatic ketones with certain glycols in the presence of acid dehydrating catalysts[34]. Before this, only a few examples of the condensation of acetone itself with polyhydroxy-compounds were known[35]. The problem of the production of cyclic ketals of this type was solved by Salmi, by showing that the reason for the lack of success of several authors who had tried to effect the condensation of 1,3-glycols with ketones was because the water is an inhibitor for the reaction. Salmi himself proposed azeotropic distillation of the water formed and by using this method obtained good yields of 1,3-dioxans, effecting the condensation of trimethyleneglycol or 1,3-butyleneglycol with ethyl methyl ketone, pinacolin, cyclopentanone, and acetoacetic ester. The catalyst in Salmi's studies was *p*-toluenesulphonic acid[18]. Many alkyl[36-42], polyalkyl[9,15,21,25,26,43-49], aryl[20,21,50-66], halogenoalkyl[10,21,67-77], hydroxy[78-87], nitro-[88-95], alkoxy-[77,96,97], and alkoxyalkyl[98-100], unsaturated[77,101-104], carbonyl-substituted[105,106], polycyclic[77,107-110], cyano-[77,111], and amino-[48,49,55,56,112] 1,3-dioxans were obtained by this method. Some variants of the method are of interest. Thus, a process has been patented[114] in which a mixture of formaldehyde and 1,3-butyleneglycol is passed continuously over an acid catalyst at high temperature. In this way a mixture of substituted dioxans and dioxolans[115] was obtained from glycerol:



(2)

Still more complex mixtures are obtained from higher alcohols and aldehydes[116,117]. Hill and Carothers[118] obtained tetramethyleneglycol formal and showed that other polyformals are successfully formed in the reaction of glycols of the type $HOCH_2[CH_2]_nCH_2OH$ with formaldehyde in the presence of acid catalysts.

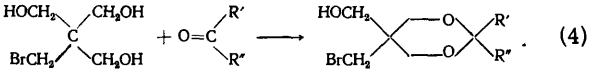
In 1961 Schipper and coworkers[88] proposed an original method for obtaining amino-substituted 1,3-dioxans:



(3)

Another method for obtaining amino-substituted 1,3-dioxans was proposed by Yasnitskii and coworkers in 1963[29-31]. They condensed chloroacetaldehyde with polyhydric alcohols in the presence of cation-exchange resins. The chloromethyl derivatives of 1,3-dioxans thus obtained are comparatively readily converted into alkylaminomethyl derivatives, owing to the rather high lability of the chlorine atom.

Piganiol and coworkers[10,50] obtained interesting, phamacologically active 1,3-dioxans (V) with two functional groups, by condensing pentaerythritol monobromohydrin [2-bromomethyl-2-hydroxymethylpropan-1,3-diol (Ed. of Translation)] with various aldehydes and ketones:



(4)

Of the variants of the method for the production of ketals, note must be made of the work of Kuhn[119], who used unsaturated ketones and esters of laevulinic acid for the production of 1,3-dioxans. By studying a different type of compound containing a ketone group in this reaction, Kuhn succeeded in showing that ketals of the 1,3-dioxan type can be obtained from any α-, β-, or γ-keto-acid except those in which there is a double bond next to the carbonyl group. When that is so ketals are not formed.

2. Production of 1,3-Dioxans by the Reaction of Aldehydes with Unsaturated Compounds

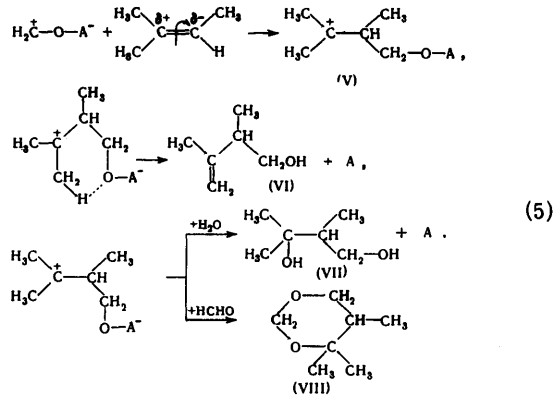
In 1917 Prins first studied the reaction of styrene, pinene, camphene, and anethole with formaldehyde in the presence of sulphuric acid as a catalyst[120]. Since then this reaction, named the "Prins reaction", has obtained wide application. An especially large number of papers devoted to it appeared at the end of the nineteen-thirties[121] after the development of improved procedures for cracking petroleum, which made accessible many unsaturated hydrocarbons. At the same time industrial methods of obtaining aldehydes from hydrocarbons were also developed.

In the condensation of alkenes and some other unsaturated compounds with aldehydes in the presence of aqueous solutions of mineral acids alkyl-1,3-dioxans and butan-1,3-diols are formed. The ratio of the reaction products can be varied by changing the concentration of the catalyst and the temperature of the process.

For a long time the mechanism of the Prins reaction was considered debatable. Several hypotheses were advanced[122-127]. A more or less general standpoint has recently been developed. It is thought that a polarised complex of formaldehyde with the catalyst adds to the alkene according to the Markovnikov rule, Eqn. (5):

$$HCHO + A \rightleftarrows H_2\overset{+}{C}-O-A^-,$$

where A is the catalyst: acid, $SnCl_4$, or other suitable substances.



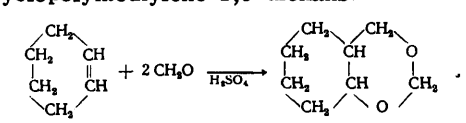
(5)

During this, an intermediate compound (V) is formed, which can then react either as a six-membered ring, or with other components of the reaction mixture. In the first instance an unsaturated alcohol (VI) is formed. In the second, a 1,3-glycol (VII) is formed when the reaction is with water; in the reaction with formaldehyde the 1,3-dioxan (VIII) is formed. Recently there have been many studies of the products of the Prins reaction[128-133]. 1,3-Dioxans can be obtained by this method from both linear and cyclic alkenes. Fitzky[134] and Ritter[135] investigated the preparation of alkyl-1,3-dioxans by the condensation of formaldehyde with propene, 2-methylpropene, trimethylethylene [1,2-dimethylpropene] pent-2-ene, and di-isobutylene [2,2,4-trimethylpentenes (Ed. of Translation)] in the presence of various acid catalysts. The best yields were obtained on using sulphuric acid as catalyst.

Later patents testify to the perfection of the commercial process for the synthesis of 1,3-dioxans[136-143]. A selective method for obtaining 4,4-dimethyl-1,3-dioxan by the reaction of a mixture of hydrocarbons with five or less carbon atoms with formaldehyde in the presence of H_2SO_4 (or H_3PO_4) at 10–85°C and atmospheric or elevated pressure has been patented[144,145]. An interesting variant of this method uses cation-exchange resin[146].

Mottern[147] used the Prins reaction for the selective removal of alkenes having branching at the double bond from fractions obtained as a result of petroleum distillation.

Cyclohexene and other cyclic alkenes also react with formaldehyde at 60–80°C in the presence of sulphuric acid, forming cyclopolymethylene-1,3-dioxans:



(6)

Aldehydes react selectively with ethylenic bonds of arylalkenes (for example, styrene), forming phenyl-1,3-dioxans. Here the catalysts are sulphuric acid[149-151], a solution of sulphuric in acetic acid[152-154], dilute hydrochloric acid[153,155], phosphoric acid[151,156,157], certain salts of hydrochloric acid[158], and other acid catalysts[159-161].

Good methods for obtaining phenyl-1,3-dioxans from arylalkenes and formaldehyde in the presence of sulphuric acid were developed by Shreiner[162], Shortige[163], Emerson[153,164], Beets[149,150,165,166] and their coworkers. Arylalkenes can be replaced by arylalkylcarbinols, but the yields of the dioxans are then reduced to 5–20%.[165-167]

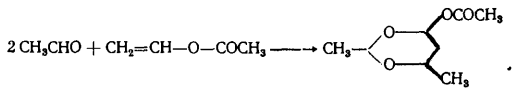
The terpenes (for example, pinene, limonene, camphene, cedrene, allo-ocimene, myrcene) react with formaldehyde in the presence of hydrochloric, sulphuric, and *p*-toluenesulphonic acids to form condensation products and resins, but their nature has not been determined with sufficient precision[152,168,169].

Some substituted alkenes, especially unsaturated halides and ethers, can undergo the Prins reaction, forming various 1,3-dioxans. The condensation of allyl chloride with formaldehyde at 0°C in the presence of concentrated sulphuric acid leads to the production of 4-chloromethyl-1,3-dioxan[170]. Dimethylallyl ethyl ether and formaldehyde readily react in the presence of 25% sulphuric acid at room temperature to form 5-ethoxymethyl-4,4-dimethyl-1,3-dioxan in 73% yield[171].

It must be noted that in the condensation of unsaturated carbonyl compounds (aldehydes, ketones, acids, and their derivatives with formaldehyde) the formation of 1,3-dioxans takes place with some difficulty; unsaturated alcohols and esters react with formaldehyde in the presence of acid catalysts, but the reaction products are difficult to identify, evidently owing to further reaction of the aldehyde with the hydroxyl groups of the molecule.

Recently published patents describe the reaction of branched alkenes, tertiary alcohols, and halogeno-derivatives with aldehydes in the presence of boron trifluoride, which leads to the formation of substituted 1,3-dioxans[172].

In the presence of metallic sodium, acetaldehyde condenses at 0°C with vinyl acetate, as a result of which 6-acetoxy-2,4-dimethyl-1,3-dioxan is obtained[173]:

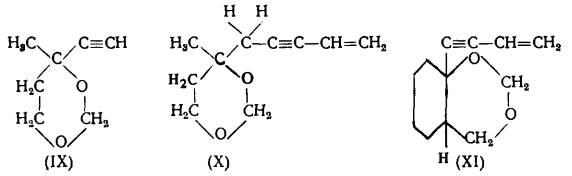


(7)

This reaction is evidently strictly specific both in regard to the reagents and also the conditions used. Cresham and Grigsby[174] studied the condensation of butadiene with formaldehyde in the presence of acid catalysts and hydroquinone (an inhibitor of polymerisation) at 100–120°C. They obtained 4-vinyl-1,3-dioxan in 30% yield. However, according to other results[152] this reaction leads to the formation of a very complex mixture of substances. Evidently the reason for Cresham and Grigsby's success was the use of a polymerisation inhibitor. The Prins reaction with other diene hydrocarbons has not been studied.

Matsoyan and Saakyan's interesting work[175] was published at the end of 1963; it was devoted to the reaction of formaldehyde with enynic and dieneyne hydrocarbons under the conditions for the Prins reaction. It appeared that the latter react selectively at the double bond with the formation of ethynyl- and vinylethynyl-1,3-dioxans. Thus on heating isopropenylacetylene [2-methylbut-1-en-3-yne] with formaldehyde in the presence of 40% sulphuric acid at 60–80°C 4-ethynyl-4-methyl-1,3-dioxan (IX) is formed. Formaldehyde reacts analogously with dienes, the reaction being directed exclusively to the substituted double bond of the divinylacetylene hydrocarbon. The condensation of 5-methylhexa-1,5-diene-3-yne and 5-methylhepta-1,5-diene-3-yne with formaldehyde in the presence of 40% sulphuric acid leads to the formation of 4-methyl-4-vinylethynyl-1,3-dioxan (X; R = H) and 4,5-dimethyl-4-vinylethynyl-1,3-dioxan (X; R = CH_3). Under analogous conditions 1-vi-

nylethynylcyclohexene and formaldehyde gave a bicyclic dioxan (XI):

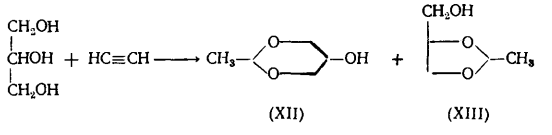


(8)

A quite interesting modification in the Prins reaction was the replacement of mineral acids or their derivatives as catalysts by sulphonic cation-exchange resins[176]. The use of KU-1 cation-exchange resin† for the production of 4-phenyl-1,3-dioxan in the condensation of styrene with formaldehyde greatly facilitates the purification of the reaction product and makes possible the repeated use of the catalyst at the same yield[177] (up to 80%). Similar results have also been obtained for other cation-exchange resins[178,179].

3. Production of 1,3-Dioxans from Acetylene and Polyhydroxy-Compounds

The first information about this method of synthesis was reported in a German patent[180]. As a result of the reaction of a warm solution of glycerol with acetylene in the presence of mercury(II) chloride a mixture of five- and six-membered heterocyclic compounds is obtained, of the *m*-dioxan and dioxolan type. Later, Hill and Hibbert, using the results of Newland on the reaction between acetylene and alcohols in the presence of sulphuric acid and mercury(II) sulphate[181], found that acetylene reacts under these conditions with glycerol to form substituted 1,3-dioxans[182]. The same investigators showed that as a result of this reaction a mixture of five- and six-membered heterocyclic compounds is obtained: 5-hydroxy-2-methyl-1,3-dioxan (XII) and 4-hydroxymethyl-2-methyl-1,3-dioxolan (XIII):

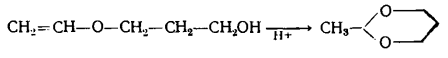


(9)

The details of the cyclisation of this type were found by Hill and Pigeon[183], who showed that in the reaction of acetylene with glycol the vinyl ether

$$CH_2=CH-O-CH_2-CH_2OH,$$

is formed, which in the presence of traces of sulphuric acid is rapidly rearranged into a cyclic ether. Thus under the stated conditions hydroxypropyl vinyl ether is converted into 2-methyl-1,3-dioxan:

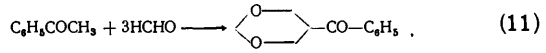


(10)

† KU-1 is a difunctional, strongly acid cation-exchange resin with $-SO_3H$ and –OH active groups, prepared by polycondensation of *p*-phenolsulphonic acid with formaldehyde in acid (Ed. of Translation).

4. Production of 1,3-Dioxans by Various Condensations with Formaldehyde

Fuson and coworkers[184] obtained 5-benzoyl-1,3-dioxan by the action of paraform on acetophenone in methanol solution in the presence of potassium carbonate:

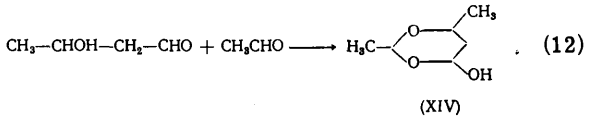


(11)

This type of alkaline condensation is unusual, since it is generally accepted that acetals are obtained in the presence of acid catalysts. However, this example is not unique. Thus, Bergman and Miekely[185] isolated cyclic formals produced by the reaction of the simplest primary amines with an excess of an aqueous solution of formaldehyde at low temperature. Finally, alkaline catalysts are used for obtaining cyclic formals from mixtures of aldehydes.

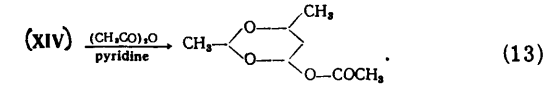
5. Production of 1,3-Dioxans as a Result of the Polymerisation of Aldehydes

In 1935 Shilov[186] reported the formation of 6-hydroxy-2,4-dimethyl-1,3-dioxan in the polymerisation of acetaldehyde in the presence of sodium hydroxide. This problem was developed further in the studies of Späth and Schmid[187], in which the properties of aldol and its derivatives were studied. According to the results of these authors, the monomer of aldol is seldom obtained, except for those instances when the aldol condensation is carried out at high temperature. Evidently, in many instances the aldol reacts as a bimolecular compound. Späth and his coworkers[188] concluded that the presence of the 1,3-dioxan structure in the dimer of aldol is due to intramolecular cyclisation of the hemiacetal formed intermediately. Consequently, simple aldehydes should react with monomeric aldol, forming hemiacetals, which are cyclised into 1,3-dioxans. On heating acetaldehyde with aldol in a sealed tube at 100°C, these authors obtained 6-hydroxy-2,4-dimethyl-1,3-dioxan (XIV):



(12)

Hanschke[189] subsequently produced further proof of the correctness of Späth's hypothesis. The crude product of the polymerisation of acetaldehyde was acetylated with acetic anhydride in pyridine. The acetate isolated seemed identical with the substance obtained by Späth in the acetylation of (XIV):



(13)

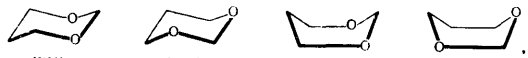
Hence in the polymerisation and condensation of aldehydes, beginning with the simplest, a variety of compounds having the 1,3-dioxan structure are formed, including polymerised 1,3-dioxans[190].

III. STEREOCHEMISTRY OF 1,3-DIOXANS

The stereochemistry of 1,3-dioxans has been little studied, nevertheless its development is extremely important for the further perfection of general stereochemical

ideas, in particular for the development of conformational analysis. Being heterocyclic analogues of cyclohexane (the "pseudocyclohexane ring"), 1,3-dioxans have several important peculiarities. Thus, the presence of oxygen atoms in the 1- and 3- positions of the six-membered ring leads to weakening or, in any case, to a change in the character of the non-bonded interactions of the 1–3 type in this ring. This makes the boat configuration more probable and favourable in this series, in comparison with the boat in the cyclohexane series. Although this in itself is extremely interesting and new, it is far from being the only peculiarity of the stereochemistry of the system being studied. The stereochemistry of 1,3-dioxans has made only the first steps but they already merit attention.

Most authors now ascribe to 1,3-dioxan itself (I) the chair conformation (XV). The following is the basis for this. As long ago as 1937 Otto[191], having measured the dipole moment of (I) and having been satisfied that it is small ($\mu = 1.91$ D) suggested that the most probable conformation of (I) should be the chair form. It is easy to see that forms (XV) and (XVI) are identical, which cannot be said about the boat, of the two possible forms of which (XVII) can be called the symmetrical, and (XVIII) the non-symmetrical boat:



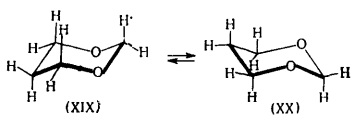
(XV) (XVI) (XVII) (XVIII)

Otto, however, did not make any calculations, but restricted himself to only a qualitative appraisal of these conformations.

Later, Arbuzov[192] pronounced in support of the correctness of Otto's hypothesis. He calculated the dipole moments of the hypothetical planar form (I) ($\mu_{calc} = 1.33$ D), the chair form ($\mu_{calc} = 1.91$ D), and of one of the boat forms ($\mu_{calc} = 2.34$ D).

The information obtained by dipole moment measurements about the conformation of 1,3-dioxan was confirmed by additional results obtained on the basis of an examination of the NMR spectra of this compound[193–195].

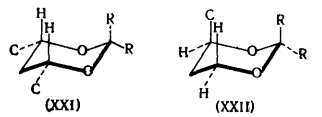
The singlet nature of the peak of the axial and equatorial protons shows the repeated changes of one chair form into the other, (XIX) $\rightleftharpoons$ (XX), hence on average in time the axial and equatorial protons of all the CH_2 groups of the ring become equivalent:



(XIX) (XX)

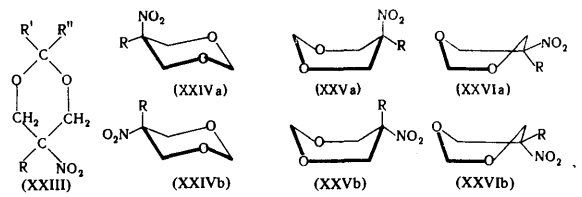
Barbier and coworkers come to the same conclusion in their work, by stating that 1,3-dioxan is present in the chair form and there is a constant chair–chair inversion (XIX) $\rightleftharpoons$ (XX). Consequently Barbier's work confirms completely and independently the interpretation of the spectrum which was given above and was proposed by Samitov.

If the problem of the conformation of (I) can evidently be considered as solved, the problem of the predominant conformations of substituted 1,3-dioxans, the configuration and conformations of the stereoisomeric derivatives of 1,3-dioxan is far from clear and should be decided independently for each separate instance. Thus the chair conformation is evidently favourable for some substituted 1,3-dioxans. This is supported by the theoretical works of Barker and coworkers[196,197], Mills[198], and Klyne[199]. These authors theoretically considered the hypothetical formation of definite types of ring in 1,3-dioxans. All the authors mentioned started from the fact that the most stable conformation of the initial polyhydric alcohol exhibits a zigzag-shaped structure of the carbon skeleton. If this is so then, according to Barker, on closure of the ring the latter can and should be formed by two hydroxyl groups present on the same side of the Fischer projection. This means that as a result of such a reaction the dioxan ring must of necessity be closed with two equatorial substituents in the 4- and 6- positions. This is termed the β-*C*-ring (XXI). The other variant of the ring, the β-*T*-ring (XXII) is more difficult to form, in the opinion of the above authors. All this fits in with the general rules of conformational analysis. However, it should be noted that the authors mentioned[196–199] at once reject the boat form for such molecules without discussing its possible variants:



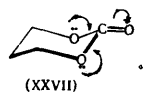
(XXI) (XXII)

Moreover, this is evidently not always true, since a consideration, by the present authors, of this conformation on Stewart–Brigleb models showed that the boat, especially the non-symmetrical boat (XXIII) in the series being considered is incomparably more favourable than in the cyclohexane series. Experimental investigations devoted to this problem are contradictory. There are studies in which the conclusions support the predominance of the chair conformation in substituted 1,3-dioxans. Studies have also been published in which it is stated that substituted 1,3-dioxans exist predominantly in the boat conformation. Of the former, mention must be made above all of the great review paper of Urbanskii[200] at the Butlerov symposium in 1961, in which amongst other data devoted to the study of the stereochemistry of six-membered heterocycles, information was given on the study of the conformation of the 5-nitro-substituted 1,3-dioxans of formula (XXIII). To find the preferable conformations of these substances the dipole moments of all possible conformations of (XXIII) were calculated. These values were then compared with the experimental results.



(XXIII) (XXIVa) (XXIVb) (XXVa) (XXVb) (XXVIa) (XXVIb)

For more complex derivatives of (I) the study of the dipole moments for proof of the conformations becomes difficult[201,202]. Thus dipole moments were calculated for the planar form, and the chair and boat forms of trimethyleneglycol carbonate (XXVII). They were 4.24, 3.56, and 3.28 respectively. The value found is 5.28.[192] Arbuzov[192] explains this anomaly by electronic displacements in the molecule of (XXVII):



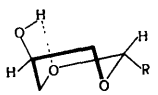
(XXVII)

However, this statement needs additional verification, since it is not confirmed quantitatively.

Most of the information now published shows that the chair conformation is most probable for substituted 1,3-dioxans. Of the studies on which it is maintained that substituted 1,3-dioxans exist in the boat form, mention can be

made of the work of Foster and coworkers [203-206] and that of the authors of the present article [207,208]. These are connected with the use of spectroscopic methods of investigation. Unfortunately, there have been few studies of the 1,3-dioxans by ultraviolet, infrared, Raman, and NMR spectroscopy.

The study of 1,3-dioxans by ultraviolet spectroscopy showed that they absorb in the far vacuum region of the spectrum. However, the number of works devoted to the study of the vacuum ultraviolet spectra of 1,3-dioxans is very small and the conclusions [209-212] do not allow a judgement about the stereochemistry of these substances to be made on their basis. Still fewer papers are devoted to studies of the Raman spectra. There is only one paper [213] on this region and from this it is possible to draw only insignificant information. The study of the infrared spectra of 1,3-dioxans began comparatively recently [214,215]. The first studies confirmed the presence in the infrared spectra of substituted 1,3-dioxans of bands of complex structure but until recently there was no success in finding the number of characteristic bands, without speaking of more far-reaching investigations. However, papers devoted to a more systematic study of this problem have recently appeared [207,208]. Thus, Ledwoch [216] succeeded in finding a set of characteristic bands for the 1,3-dioxan ring (ν = 1025–1035, 1070–1110, 1160–1175, 2745–2795 cm^{-1}), and Foster and coworkers [217-220] found, in a study of the infrared spectra, that some of the *trans*-2-alkyl-5-hydroxy-1,3-dioxans and substituted 5-hydroxy-1,3-dioxans exist in the preferential conformation of the non-symmetrical boat (XXVIII). The reason for the existence of this form was thought by Foster to be that the large group R experiences less non-bonding interactions in this conformation than in the chair. Moreover, the boat (XXVIII) is stabilised due to the formation of a hydrogen bond:



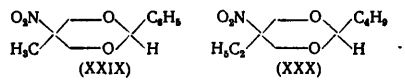
(XXVIII)

Results which show the possibility and permissibility of the boat conformations in a series of 2-substituted 5α-alkoxyethyl-5-alkyl-1,3-dioxans were obtained by the present authors in a study of the NMR spectra of these compounds. These investigations are analysed below.

From all that has been stated it can be concluded that the conformations in the 1,3-dioxan series are somewhat different from the cyclohexane series. Whereas 1,3-dioxan itself evidently exists in the chair form, its derivatives can have not only the most favourable chair conformation, but also the boat conformation, which in the series being considered is more favourable than in the cyclohexane series.

The second important problem of the stereochemistry of the 1,3-dioxans consists in finding the configuration of the geometrical isomers of the 1,3-dioxans. It is easy to see that any (apart from *gem*-substituted) disubstituted 1,3-dioxans, and also tri- and more substituted 1,3-dioxans, should be mixtures of geometric isomers, which often are also diastereomers. This aspect of the stereochemistry of the 1,3-dioxans has been little studied. Very few authors have succeeded in resolving 1,3-dioxans into stereoisomers, and still fewer have firmly established the configuration of these isomers.

In 1928 Hibbert and Carter [221] succeeded in finding experimentally the presence of *cis-trans*-isomers in 2-(-*p*-nitrophenyl)-5-hydroxy-1,3-dioxan and its derivatives (5-methyl, 5-benzoyl, and 5-nitrobenzoyl). In 1942 Verkade and van Roon [84] separated the geometric isomers of 5-hydroxy-2-phenyl-1,3-dioxans. A year later Zenkus [112] synthesised 5-methyl-5-nitro-2-phenyl-1,3-dioxan (XXIX), which was separated into stereoisomers owing to a difference in the solubility of the latter in benzene–cyclohexane mixture. The melting points of these isomers are 118° and 78.4°C respectively. These isomers were then reduced to amino-derivatives, which also seemed stereoisomers and melted at 84° and 48.2°C respectively. A similar operation was also carried out on 2-butyl-5-ethyl-5-nitro-1,3-dioxans (XXX):



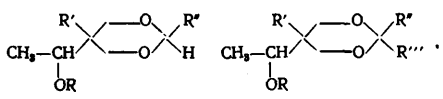
(XXIX) (XXX)

A characteristic for all the older works mentioned was that only the crystalline 1,3-dioxans were separated by fractional crystallisation and the authors refrained from firm statements about the configuration of the substances obtained. In recent years the studies in this field were extended and chromatographic methods were applied to the investigation of stereoisomerism. Thus, Rondestvedt [21] reported on the separation, by use of gas–liquid chromatography, of the geometric isomers of some of the 1,3-dioxans they had synthesised. It is quite interesting that this author applied the method of conformational analysis to the investigation of the systems they synthesised and advanced the hypothesis that the largest substituent should occupy an equatorial position in the molecules of separate isomers. Rondestvedt tried to use infrared spectroscopy for studying these problems. The preparative separation of the isomers, carried out in three instances, was again by fractional crystallisation.

Portoghese and Smissman [222] and later Smissman and coworkers [223], in studying the stereochemistry of the Prins reaction connected the stereoisomerism of 1,3-dioxans with that of the related 1,3-diols. The authors of these works were some of the first to use nuclear magnetic resonance for studying this problem. They succeeded in showing that the Prins reaction is characterised by *cis*-addition in several instances. In studying this process, they found in passing the configuration of some aryl-substituted 1,3-dioxans. Nuclear magnetic resonance was also used by Bagget and coworkers [224] in a work devoted to a proof of the configuration of the stereoisomeric derivatives of 5-hydroxy-1,3-dioxan. In this work hypotheses about the predominant conformations of these stereoisomers were advanced in which it stated that both the *trans*- and the *cis*-isomers have the chair conformation, but whereas the *trans*-isomer does not exhibit the chair–chair type of inversion, the *cis*-isomer does. The latter assumption was made on the grounds that the peak of the protons found in the 4- and 6- positions of the molecule of the *cis*-isomer was a singlet, that is, showed their equivalence. Possibly, however, this statement is not completely correct and the apparent equivalence of the 4- and 6-axial and equatorial protons is due to another reason, as will be discussed below.

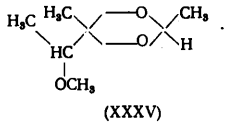
In a series of later studies [216-219] it was suggested that stereoisomers exist in synthesised mixtures of 1,3-dioxans. Quite recently Kaplan [87] succeeded in resolving some 2-alkyl-5-ethyl-5-hydroxymethyl-1,3-dioxans into stereoisomers by gas–liquid chromatography.

In a series of published investigations Bogatskii and coworkers[207,208] examined the problem of the stereochemistry of 2-substituted 5-α-alkoxy-5-alkyl-1,3-dioxans, of the type of (XXXI) and (XXXII):



(XXXI) (XXXII)

During the course of these investigations, initially by gas–liquid chromatography and proton magnetic resonance, the existence of geometrical isomers in substance of type (XXXI) was demonstrated[99,100], after which they were separated into individual isomers by rectification on efficient columns. This was the first example in the literature of the separation of the derivatives of 1,3-dioxans into stereoisomers by rectification. The purity of the isomers obtained was determined chromatographically and was 95 to 99%. To establish the configuration and conformation of the individual isomers, dipole moments and NMR methods were then used. The authors succeeded in showing that the low-boiling isomers of (XXXI) are *trans*-isomers (XXXIII)‡, which exist in the predominant conformation of a chair, and the high-boiling are *cis*-isomers (XXXIV)‡ which exist in the predominant conformation of the non-symmetric boat. The NMR spectra showed that in the specimens examined there was absolutely no sign of inversion of the conformations. A study of the NMR spectra of *cis*- and *trans*-5α-methoxyethyl-2,5-dimethyl-1,3-dioxans raised no doubts on the non-equivalence of the axial and equatorial protons of the methyl groups, which shows the absence of inversion. Comparison of the calculated and measured values of the non-equivalence shows the chair conformation. This conclusion, obtained on the basis of a study of NMR spectra was confirmed by studying the dipole moment. Actually, the dipole moment of the *trans*-isomer (XXXV) was found to be $\mu = 1.15$ D. The value calculated for the chair conformation is $\mu = 1.16$ D.



(XXXV)

A characteristic feature of the spectrum of the *cis*-isomer is the absence of a peak with an anomalously low value of the chemical shift and the singlet nature of the peak of the protons of the $C_{(4)}$ or $C_{(6)}$ CH_2 group. This singlet nature cannot be the result of inversion of conformation, since other regions of the spectrum do not show averaging of the shifts of the axial and equatorial substituents. A comparison of calculated and measured values of non-equivalency shows that such phenomena should take place in the non-symmetrical boat configuration where the calculated non-equivalence of the $C_{(4)}$ protons is $\delta = 0.4$ p.p.m., and that of the $C_{(6)}$ protons $\delta = 0.16$ p.p.m. Conclusions about the configuration *cis*- and the conformation of non-symmetrical boat are in this instance also confirmed by a study of the dipole moments. In *cis*-(XXXV) the dipole moment was found to be $\mu = 2.60$ D and that calculated for the non-symmetrical boat is $\mu = 2.56$ D.

These conclusions about the configuration and conformations of (XXXI) were then confirmed by studying the kinetics of hydrolysis of these isomers, which showed that the low-boiling isomers are hydrolysed much more slowly than the high-boiling ones and the influence of a substituent is greater on the hydrolysis of (XXXIII) than on the hydrolysis of (XXXIV). It is easy to see that this agrees with the results obtained in relation to the configuration and conformation of these stereoisomers.

In the series of stereoisomeric (XXXI) we succeeded in observing a linear relation between the difference in boiling points of the *cis*- and *trans*-isomers (Δt) and the number of carbon atoms in the (XXXI) molecule. Such a relation had been found by Kazanskii and Liberman in the cyclohexane series. This confirms the configurative relationship between the 1,3-dioxan series and the cyclohexane series. However, it is still more interesting that there is also a linear relation between the ratios of the hydrolysis constants of the stereoisomeric (XXXI) and the number of carbon atoms in the same series. Consequently, the dependence of Δt on the number of atoms is not fortuitous but is connected with the extremely intimate configurative features of these compounds.

All the information given above shows that work in this field of study of the stereochemistry of the 1,3-dioxans is developing rapidly and the results obtained up till now show the presence of a trait of similarity and at the same time a series of essential differences between these compounds and cyclohexane. Evidently, 1,3-dioxan systems are a convenient model for studying the problem of the characteristics of the boat conformations.

While this article was being considered by the Editorial Board we were undertaking investigations[338-340] which confirm the conclusions concerning the stability and extensive distribution in this series of the boat conformation and the marked favourability of the $C_{(6)}$ axial position in the 1,3-dioxan ring compared with the cyclohexane rings. It is easily established that the 5-C-axial valency in these systems is unique owing to the considerable weakening of the 1,3-interaction, since there are oxygen atoms in positions 1 and 3 of the pseudocyclohexane ring[339].

The present authors conclude that the ketals of this series are characterised by the presence of a non-symmetric boat conformation, or twist-conformation[338-340]; they have formulated an empirical rule according to which in 1,3-dioxan systems in those instances when inversion of the conformation of the ring is impossible or greatly hindered for steric reasons, the geometric isomers tend to take on the conformation (chair, symmetric or non-symmetric boat, or twist-conformation) with di-equatorial position of the largest substituents or such configuration in which one of the largest substituents occupies a $C_{(6)}$-axial position[339].

It should be noted that interest in the conformational problems in the 1,3-dioxan series is increasing continually, as is shown by the studies[341-345], whose results confirm the above conclusions and the empirical rule given.

IV. CHEMICAL CHANGES OF 1,3-DIOXANS

The chemical changes of 1,3-dioxans are rather varied, but a common feature of them is that, like the reactions of acetals and ketals, they are modified by the presence of a cyclic structure.

1. Hydrolysis and Alcoholysis

The hydrolysis of 1,3-dioxans is effected comparatively readily, although cold water and dilute and cold solutions

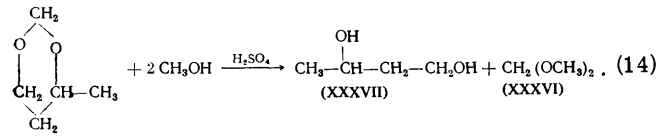
‡ Formulae (XXXIII) and (XXXIV) are not given in the Russian (Ed. of Translation).

of alkalis have little action on 1,3-dioxans[225,226]. However, in an acid medium 1,3-dioxans, like other acetals, are readily hydrolysed in the cold, even extremely dilute solutions of acids being sufficient for this[227-229]. As for all similar reactions of acetals, the hydrolysis of 1,3-dioxans in acid medium is reversible. Therefore it is not profitable to obtain 1,3-diols from 1,3-dioxans since the yield of the latter does not exceed 10–20%.[230,231] True, there are indications that the hydrolysis equilibrium can be shifted to the side of the formation of diols, by bonding the aldehydes formed by chemical means or by carrying out the hydrolysis under pressure[232].

In recent years more and more attention has been paid to the theoretical examination of the hydrolysis of 1,3-dioxans. Dilatometric[233-237], titrimetric[238-240], and spectrophotometric[241-243] methods of studying the kinetics of the hydrolysis of 1,3-dioxans have been developed and employed with success. We stated above the possibility of using a study of the hydrolysis for proving the configuration and conformation of stereoisomeric 1,3-dioxans. Of the studies of the mechanism of this reaction we can single out that of Bender and Silver[244], where the authors succeeded in finding that the rate of hydrolysis of certain substituted 1,3-dioxans in the pH range from 3 to 6 is independent of the hydrogen-ion concentration.

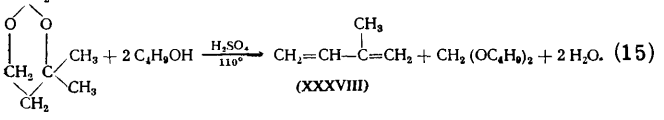
Hydrolysis of the cyclic ketals of the 1,3-dioxan type has been little studied but there are indications that six-membered ketals are less stable than five-membered[245,246], according to conformational considerations. This problem was discussed in the previous section of the present article.

Alcoholysis of 1,3-dioxans leads to the production of diols or alkenes in good yields. Thus on boiling 1,3-dioxans with methanol in the presence of sulphuric acid the splitting of the dioxan takes place very readily, in view of the fact that the methylal formed (XXXVI) is continually removed from the reaction[247,248].



(14)

When the reaction proceeds in methanol as medium its chief products are a glycol (XXXVII), whereas in alcoholysis in the presence of higher alcohols acetals (or formals) of these alcohols are left in the reaction mixture and are, together with diols, the main reaction products. Very often under these conditions the glycols are dehydrated with the formation of conjugated dienes as is shown in Eqn. (15). Consequently, the process considered can serve as a convenient method for obtaining conjugated dienes of type (XXXVIII):[249]

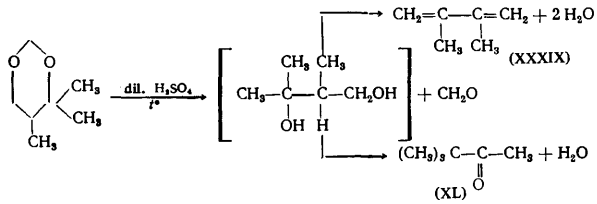


(15)

However, conjugated dienes can be obtained from the 1,3-dioxans without alcohols being present. It has been shown[250] that on boiling substituted 1,3-dioxans with aqueous solutions of mineral acids (1–5%) they are converted directly into dienes. This reaction finds industrial application and many variations of this method have been patented.

It was stated above that dioxans are stable under the action of alkalis in the cold, yet hot alkali solutions can cleave the 1,3-dioxan ring, as also can hot water[252].

An anomaly observed in the course of this reaction merits attention. Thus in the hydrolysis of 4,4,5-trimethyl-1,3-dioxan, in addition to the usual reaction products, a diene (XXXIX) and formaldehyde, ketones of the pinacolin type (XL) are also formed:



(16)

This anomaly can be explained in passing by the occurrence during the course of the reaction of hydrolysis and dehydration with a pinacol rearrangement of the diol formed, Eqn. (16).[253]

2. Thermal and Catalytic Decomposition

This section deals with a wide range of catalytic conversions of 1,3-dioxans connected with cleavage of the ring and in this sense the reactions being considered are close to the previously described hydrolytic cleavage of the 1,3-dioxan systems.

Catalytic pyrolysis of substituted 1,3-dioxans over dehydrating catalysts leads directly to the production in good yields of conjugated diene hydrocarbons. This is the most suitable method industrially for the production of conjugated dienes, in particular isoprene, since the dioxans themselves which are used for these reactions are accessible and cheap, seeing that they are obtained from alkenes by the Prins reaction. There is an extensive literature on this subject, still growing at the present time[254-273], and mainly devoted to the production of isoprene; the different variants of the method mentioned are usually patented.

Several catalysts have been proposed for this reaction. Various authors have at different times proposed as catalysts a mixture of H_3PO_4 or $H_4P_2O_7$ with phosphorus furnace slags, kaolin, or bentonite. The catalyst mass was activated by passing steam at 150–300°C under pressure and was regenerated by passage of an air–nitrogen mixture at 400–600°C.[254-256]

Other authors have used oxide catalysts[256,257], a mixture of boric and phosphoric acids[258], zinc chloride and manganese chloride[259,260], various catalysts based on phosphoric acid[261-264], and several other acid catalysts of the most diverse nature[266].

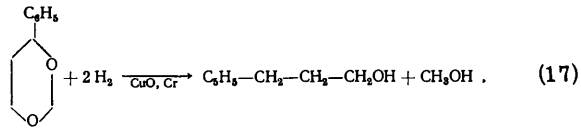
The French authors Coussemant, and Hellin and their coworkers[267-272] have recently made extensive investigations in this field; they studied a series of catalysts based on phosphoric acid and obtained patents on various versions of the industrial production of isoprene from 4,4-dimethyl-1,3-dioxan.

Hamamoto and Mizutani[274] carried out a serious investigation by comparing oxide catalysts, the salts of various metals, and acids, borate catalysts, and catalysts based on phosphoric acid in this reaction[274].

The thermal cleavage of 1,3-dioxans can also take place without catalysts at 200–600°C, but the yields of the cleavage products are lower (not more than 10%). In this reaction the products are usually alkenes, formaldehyde (or other aldehydes), or CO and hydrogen[121].

3. Reduction and Hydrogenolysis of 1,3-Dioxans

The hydrogenolysis of 1,3-dioxans can be used for the synthesis of certain alcohols[275-277]. The hydrogenation of 4-phenyl-1,3-dioxan, leading to the production of 3-phenylpropanol in 85% yield, has been described:



(17)

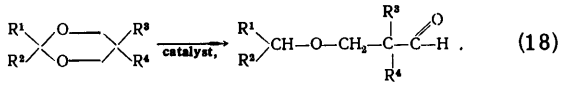
Under analogous conditions 4,4-dimethyl-1,3-dioxan is converted into isopentyl alcohol[278], and the acylated 1,3-dioxans into the corresponding β-monoglycerides[279-282].

1,3-Dioxans arylated in the 4- position are capable of reductive cleavage under the action of sodium in the presence of high-boiling alcohols, for example, di-isobutylmethanol[165-167]. Here also reductive cleavage proceeds selectively leading to the loss of oxygen attached to the $C_{(4)}$ carbon.

Finally, the possibility was recently shown of effecting the hydrogenolysis of 1,3-dioxans under the action of lithium tetrahydroaluminate[283,284] and also their reduction with the aid of organomagnesium compounds[285,286]. These reactions lead to cleavage of the 1,3-dioxan ring and the production of either alkoxy-alcohols[286] or unsaturated alcohols[285], depending on the conditions.

4. Catalytic Isomerisation and Catalytic Changes

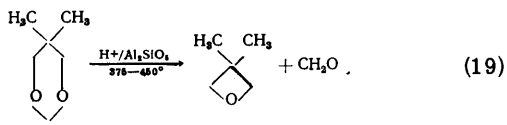
In 1961 Rondestvedt reported the finding of a new type of conversion of 1,3-dioxans—catalytic isomerisation of these substances into β-alkoxyaldehydes according to Eqn.(18)[287-289]:



(18)

This reaction takes place at elevated temperatures in the presence of weakly acid catalysts. For example, on pumice it is effected at 360–450°C and on silica gel at 250–350°C. The ease of rearrangement depends on the nature of the radicals R^1–R^4. For example, the presence of two substituents at position 5 is obligatory, or otherwise further decomposition of the reaction products takes place, into the corresponding alcohol and arylaldehyde. Moreover, it was found that electron-acceptor groups in position 2 hinder the course of the rearrangement, and alkyl and cycloalkyl substituents in the same position facilitate it.

Another interesting reaction was observed by Bartok[290], the conversion of 1,3-dioxans into the oxacyclobutane system:



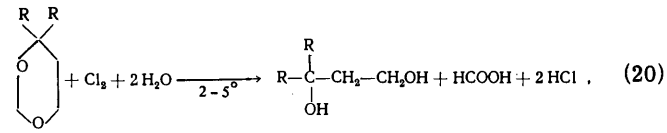
(19)

This conversion is effected on an acid cracking catalyst according to Eqn. (19) at 370–450°C and leads to the production of oxacyclobutane derivatives in 25–30% yield.

5. Halogenations

Of the halogenations of 1,3-dioxans, their chlorination has been studied better than the other reactions.

The chlorination of 4,4-dialkyl-1,3-dioxans in an aqueous medium leads to their hydrolysis with the formation of the corresponding glycols and is not accompanied by the dehydration of the latter. Evidently the unstable 4,4-dialkyl-2-chloro-1,3-dioxan is formed initially, then decomposes in the presence of water to form glycol, and formic and hydrochloric acids[291]:

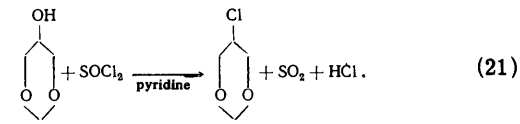


(20)

The chlorination proceeds otherwise in the absence of water. Under these conditions chlorination and bromination lead to the formation of polychloro- and polybromo-derivatives of 1,3-dioxans, which, however, cannot be purified and isolated[292].

There are interesting studies devoted to the action of various halogenating agents—phosphorus(V) chloride, thionyl chloride, etc.[60] Phosphorus(V) chloride breaks the 1,3-dioxan ring, to form trimethylene chloride[293].

Under the action of thionyl chloride on 5-hydroxy-1,3-dioxan, 5-chloro-1,3-dioxan was obtained[68,294]:



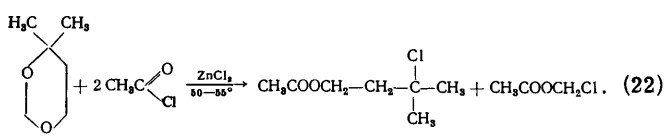
(21)

Halogenation proceeds more easily in the side-chain of substituted 1,3-dioxans. However, here difficulties are encountered since it is constantly necessary to consider the possibility of cleavage of the ring.

6. Action of Anhydrides and Acyl Halides of Organic Acids on 1,3-Dioxans

The action on 1,3-dioxans of anhydrides and acyl halides of organic acids has been little investigated, yet papers have been published which enable the course of the reaction to be predicted. Thus when acetic acid acts on 1,3-dioxan in the presence of concentrated sulphuric acid the ring is broken and the corresponding glycol diacetals are formed. In this way 5-ethyl-5-nitro-1,3-dioxan was converted into 2-ethyl-2-nitropropan-1,3-diol diacetate[295]. It is easy to understand that this reaction is related to the hydrolysis and alcoholysis, with the difference that here attack is by a glycol (not an aldehyde, as in alcoholysis). However, the reaction under consideration does not always proceed so simply. It is known that sometimes it is accompanied by side-reactions and rearrangements. For example, it is known that under the action of acetic anhydride in the presence of sulphuric acid 4-phenyl-1,3-dioxan is converted into 1,5-diacetoxy-2-hydroxy-3-phenylpentanediol[296]. Other authors, for example, Senkus[295], have described similar conversions.

Acyl halides of organic acids react with 1,3-dioxans in a similar manner. When 4,4-dimethyl-1,3-dioxan reacts with acetyl chloride, breaking of the ring and formation of the corresponding chloro-esters is observed[297]. It is interesting that the yields in this reaction are almost quantitative:



(22)

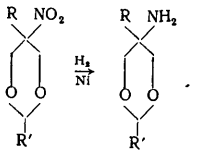
However, here also side-reactions are possible. On boiling alkyl-substituted 1,3-dioxans with small amounts of acyl chlorides in the presence of Friedel–Crafts catalysts, solid resins are obtained[298], probably formed as a result of secondary polycondensation processes.

7. Oxidation

There has been little investigation of the oxidation of 1,3-dioxans. Results have been published which show that in the photo-oxidation of 1,3-dioxan various peroxides can be obtained, depending on the conditions[299]. Oxidation for 100–120 h at 50°C gave a dihydroperoxide, and for 9–10 days at 25°C a hydroperoxide; the latter is then polymerised into a dimer. In 1964 Ikeda and coworkers published an extensive paper[300] devoted to the study of the autoxidation of 1,3-dioxans by atmospheric oxygen and also the oxidation of these substances in the presence of catalysts. The authors of this work obtained five types of oxidation product: peroxides, hydroperoxides, spirocyclic peroxides, $\alpha\beta$-unsaturated ethers, and polymers. The products were obtained in different quantities and proportions, depending on the reaction conditions; without a catalyst, the reaction was directed towards the side of the production of hydroperoxides and spirocyclic peroxides, but in the presence of traces of cobalt(II) derivatives the reaction is directed towards the side of the formation of $\alpha\beta$-unsaturated ethers and polymers, etc. However, the properties of peroxides and hydroperoxides of 1,3-dioxans are still very little investigated.

8. Conversions of Functional Derivatives of 1,3-Dioxans

The patent literature[135] states that in the catalytic reduction of nitro-derivatives of 1,3-dioxans at 110 at pressure and in the presence of Raney nickel in methanol, amino-substituted 1,3-dioxans are obtained exceptionally readily and in good yields:



(23)

Another interesting conversion of substituted 1,3-dioxans is the reaction, studied by Urbanskii and Ekshtein, of 5-nitro- and 5-hydroxymethyl-1,3-dioxans with diazo-compounds, leading to the production of derivatives of 1,3-dioxans[301,302].

In addition to these papers several have been published on the conversions of hydroxy-derivatives of 1,3-dioxans and of halogeno-derivatives[88] and on the production of substances of the 1,3-dioxan type with two keto-groups in positions 4 and 6,[303-305] and several other papers on the synthesis or conversions of functional derivatives[306-315].

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In ending the review of the chemical properties of 1,3-dioxans it must be mentioned that at present only those chemical properties of this class of compound which are related to their industrial use are receiving more serious investigation, namely the hydrolysis and catalytic cleavage of 1,3-dioxans to give conjugated dienes. Information about other properties of this group of substances is extremely scanty.

V. USE OF THE 1,3-DIOXANS

Although it is still impossible to speak of the 1,3-dioxans having such a wide industrial use as, for example, 1,4-dioxan or certain other organic compounds, the available published information shows that many of these substances exhibit extremely valuable properties.

The practical uses of 1,3-dioxans can be classified in several groups. The first is the use of 1,3-dioxans as intermediates for synthesis. In this respect the most promising application is their use for making highly pure alkadienes, 1,3-diols, and β-monoglycerides[228,247,254-273,279-282].

These problems are now receiving attention and the greatest number of works is devoted to this direction. They were characterised above in the section devoted to the chemical properties of 1,3-dioxans. According to patents, some of the 1,3-dioxans can serve as components in the synthesis of polymeric materials[316-318]. Thus 5-methyl-5-($\alpha\beta$-dihydroxyethyl)-1,3-dioxan can be used for obtaining non-saturated polyethers[67].

The second direction predicts the use of 1,3-dioxans as solvents, additives, etc.[319] It was shown that 1,3-dioxans are good solvents for resins and lacquers[121,143,320], and can be used as a solvent in the deparaffinisation of oils. Mixtures with 4,4- or 4,5-dimethyl-1,3-dioxans were especially effective[321]. 1,3-Dioxans are good solvents in Grignard reactions[322].

1,3-Dioxans are good antiknock agents to add to motor fuel and increase its octane number[321]. A derivative of spiro-di-1,3-dioxans, which contain sulphur and halogen can be used as intermediates and accelerators for the vulcanisation of rubbers. The addition of 1,3-dioxans to polymers and elastomers improves their properties, increases the elasticity of the adhesives and sealing compositions based on various resins. 1,3-Dioxans are used in the production of lubricants and cements[223,324]. 2,2-dimethyl-1,3-dioxan can be used in the hydrogenation of butadiene rubbers[325,326]. The possibility of using 1,3-dioxans as denaturing agents in alcohol, for the dry cleaning of clothes, and as addition to paints to prevent their skinning during storage[327] has been noted.

The study of the physiological activity of the 1,3-dioxans is extremely promising. The possibility of using 1,3-dioxans as disinfectants has now been shown[319,327]. Blicke and coworkers investigated some pharmacological properties of a considerable number of 2,2-disubstituted 5-methyl-1,3-dioxans and mentioned their spasmolytic and antihistamine activity[48,49,56]. Subsequently, Mel'tser and coworkers synthesised a series of di-substituted 1,3-dioxans in a search for new depressants of the central nervous system[51]. Information has been published about the sedative-hypnotic action of 1,3-dioxans[328].

According to the patent literature, some 1,3-dioxans exhibit antibiotic action[265,276,329], for example, 6-acetoxy-2,4-dimethyl-1,3-dioxan[329] or the products of condensing carboxyl compounds with 1-(p-nitrophenyl)-2-acylaminopropen-1,3-diols[276].

We have obtained results which show the antimicrobial and fungicidal ability of alkoxyalkyl-substituted 1,3-dioxans[330].

Finally, quite interesting information has been obtained about the influence of 1,3-dioxans on plant growth. According to Urbanskii[331] and ourselves[332], 1,3-dioxans stimulate plant growth, especially that of monocotyledons. 1,3-Dioxans have found application in entomology[333-337] and as insect-repellant substances[46,328,337].

Consideration of the progress in the chemistry of the 1,3-dioxans shows that in recent years chemists have paid

increasing attention to these very interesting substances. This is because of the wide possibilities for their use in the synthesis of several important organic substances, the convenience of the system as a model for stereochemical investigations and their high and varied physiological activity. It is evident that in future years we can expect a still more rapid development of the chemistry of the 1,3-dioxans.

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Progress in the Analytical Chemistry of Non-aqueous Solutions

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CONTENTS

I. Introduction 278
II. Theory of the acid-base titration of non aqueous solutions 279
III. Principles of the acid-base titration of non-aqueous solutions 281
IV. Titration in non-aqueous solutions of bases 284
V. Titration in non-aqueous solutions of acids 285
VI. Titration in non-aqueous solutions of salts 287
VII. Titration of monomeric and polymeric compounds in non-aqueous solutions 288
VIII. Analysis of industrial materials 289

I. INTRODUCTION

With the rapid development of chemistry and chemical technology, it is becoming urgently necessary to improve and develop new and more effective methods for the analysis of inorganic and organic compounds. Among the most extensively applied analytical methods, a unique position is occupied by chemical and physicochemical methods based on the titration of various compounds in a medium of non-aqueous liquid solvents and in liquefied gases[1-25]. As a result, the analytical chemistry of non-aqueous solutions has developed into an important independent branch of chemical science. Reactions in non-aqueous solutions have begun to be used not only in the familiar classical

methods of alkalimetry and acidimetry, oxidation-reduction, precipitation, and complex formation, but also in specific methods of condensation, addition, substitution, oxomercuration, etc. As a result, the range of titrimetric methods has extended and there has been a marked increase in the number of substances whose quantitative determination has been found to be possible by volumetric methods[1,5,15,17,21].

It is sufficient to point out that methods involving the titration of non-aqueous solutions can be now used for the quantitative determination of a large number of individual compounds and that the number of mixtures which can be analysed by these methods is greater than the number of mixtures which analytical chemists have learned to titrate in the 140 years since Gay-Lussac introduced the methods of volumetric analysis in aqueous solutions into analytical practice. Potentiometric, conductometric, high-frequency, spectrophotometric, polarographic, chromatographic, and other physicochemical methods for the analysis of non-aqueous solutions have found the most extensive applications[25-43].

Methods involving the acid–base titration of non-aqueous solutions of various substances exhibiting acidic or basic properties in non-aqueous media are of the greatest practical and theoretical interest. This is due to the specific influence of non-aqueous solvents on many compounds whose aqueous solutions do not exhibit acidic or basic properties. As a result, the method of acid-base titration can be used successfully for the determination of the great majority of compounds, which cannot be titrated in aqueous media. At the present time non-aqueous titrametric methods are not only widely used in scientific research, but are also successfully employed in factory laboratories for chemical analysis.

In the last 4–5 years, since the publication in "Uspekhi Khimii" [Russian Chemical Reviews] of the first review on the application of non-aqueous solvents in analytical chemistry[8], research in this area has been in the following directions: (1) the development of the theoretical principles of the analytical chemistry of non-aqueous solutions—the quantitative estimation of the influence of non-aqueous solvents on the properties of electrolytes, the study of the differentiating action of solvents, etc.; (2) the use of new organic solvents as media for titration and of new reagents for the preparation of titrant solutions; (3) the development of methods for the analysis not only of individual compounds but also of mixtures of substances which exhibit analogous properties, for example mixtures of isomers, members of the same homologous series, etc.; (4) the development of methods for the analysis of compounds which do not exhibit acid-base properties in water, for example neutral salts, unsaturated compounds, ketones, aldehydes, etc.; (5) the extensive introduction of non-aqueous analytical methods for the analytical control of the composition of intermediates and the purity of finished products; and (6) the search for new methods for the determination of the equivalence point in titrations.

II. THEORY OF THE ACID–BASE TITRATION OF NON-AQUEOUS SOLUTIONS

In the theory of the analytical chemistry of non-aqueous solutions, a particularly important position is now held by ideas on the marked influence of the nature and physical properties of the solvent, the concentration of the solution, and the nature of the dissolved substance on the state of the dynamic equilibria between the ions and molecules of the dissolved substance and the solvent. This influence affects the physicochemical properties of the dissolved substance (electrical conductivity, solubility, ability to undergo dissociation, association, complex formation, etc.), and also the direction of ion exchange reactions[44-59].

Izmailov, Shkodin, Kolthoff, Bruckenstein, Hall, and a number of other workers previously carried out detailed studies of the acid–base equilibrium in anhydrous acetic acid. Work has recently been published on acid–base reactions in acetonitrile, ethylenediamine, t-butyl alcohol, dimethyl sulphoxide, and other solvents. The studies were carried out chiefly to estimate the strengths of acids and bases by measuring K_{diss} in non-aqueous solutions.

Acid–base equilibrium in acetonitrile has been studied by Kolthoff and coworkers[60-64]. It was found that in acetonitrile, perchloric acid is completely dissociated, whereas other acids, which are strong in water, are weak electrolytes. Sulphuric, nitric, hydrochloric, and hydrobromic acids dissociate according to the equation:

$$2HAn \rightleftarrows H^+ + AnHAn^-.$$

Picric acid at low concentrations (less than 0.1 M) dissociates to H^+ and Pi^-, but at higher concentrations it dissociates according to the equation

$$3HPi \rightleftarrows H^+ + Pi(HPi)_2^-.$$

Spectrophotometric and conductometric methods have been used to determine the dissociation constants

$$K_{AnHAn^-} = \frac{[AnHAn^-]}{[HAn]\,[An^-]} \text{ and } K_{HAn} = \frac{[H^+]\,[An^-]}{[HAn]}.$$

for the above acids. The acids can be arranged in the following order of decreasing strengths in a medium of acetonitrile: $HClO_4 > HBr > H_2SO_4 > HNO_3 > HCl > HPi$.

The authors cited compare the behaviour of the acids in acetic acid and in acetonitrile, by comparing the difference in the degree of dissociation of the acids with the solvation, dielectric constant, and basic nature of the solvent, with allowance for the formation and dissociation of ion pairs involving hydrogen bonding. The calculated curves for the conductometric titration of the bases in acetonitrile shows good agreement with the experimental curves[62-64]. Acetonitrile is an excellent differentiating solvent, due primarily to its very weak acidic and basic properties.

The behaviour of a number of acids and bases in acetonitrile has also been studied by other workers[65-69]. Measurement of the electrical conductivity of bases in acetonitrile showed that the dissociation of bases such as n-butylamine, diethylamine, triethylamine, 1,3-diphenylguanidine, and others in acetonitrile is less by four orders of magnitude than that in methanol[65]. The authors cited conclude that the low dissociation of the bases in acetonitrile is due chiefly to the very weak acidic properties of the solvent and the weak tendency for solvation to take place. At a concentration greater than 5×10^{-2} M, the dissociation of diphenylguanidine takes place according to the equation:

$$2B + CH_3CN \rightleftarrows (BH : B)^+ + CH_2CN^-;$$

at lower concentrations, the dissociation takes place according to the equation

$$B + CH_3CN \rightleftarrows BH^+ + CH_2CH^-.$$

The other bases are dimerised in acetonitrile and dissociate according to the equation:

$$B_2 + 2CH_3CN \rightleftarrows 2BH^+ + 2CH_2CN^-.$$

The determination of K_{diss} for perchloric acid in acetonitrile and other nitriles gave a value of about 10^{-3}, which does not agree with Kolthoff's data[70].

Schaap and coworkers[71] studied acid–base reactions in ethylenediamine. Because of the low value of the dielectric constant of ethylenediamine (DC = 12.5), none of the acids is completely dissociated in this medium. At a concentration greater than 10^{-3} M, even strong electrolytes are present in this solvent in the form of ion pairs. The association constants for the ion pairs formed by a number of acids which are strong acids in water (HCl, HBr, and HNO_3) have been determined. Values of K_{diss} for a number of derivatives of phenol, benzoic acid, and *p*-toluenesulphonic acid in ethylenediamine have been found by the electrical conductivity method[71]. Ethylenediamine exhibits a levelling action, since for all the acids studied $pK \simeq 4$.

Fritz and Marple[72,73] studied acid–base equilibria in t-butyl alcohol. On the basis of earlier studies in alcohols and other solvents with low dielectric constants, they suggest that the dissociation of acids in t-butyl alcohol takes place with the formation of ion pairs, although this process does not take place very extensively:

$$HAn \rightleftarrows H^+An^-;\ H^+An^- \rightleftarrows H^+ + An^-.$$

Potentiometric and conductometric methods were used to measure K_{diss} for perchloric, picric, and benzoic acids and 2,4-dinitrophenol.

Study of the acid–base properties of dimethyl sulphoxide[74,75] showed that in some respects this solvent behaves like water: perchloric, hydrochloric, and sulphuric acids are completely dissociated in this medium. The order of dissociation of the other acids is different from that in water. Thus picric acid is more extensively dissociated in dimethyl sulphoxide ($\Delta pK = -2.7$) than in water, whereas acetic, benzoic, and salicylic acids ($pK = 11.4$, 10, and 6.9) are less extensively dissociated in this solvent than in water; the dissociation constant of HSO_4^- in dimethyl sulphoxide is less than that in water.

Study of acid–base equilibrium in glycols (HS represents the solvent)[76] showed that the dissociation of acids corresponds to the equation

$$HAn + HS \rightleftarrows H_2S^+ + An^-,$$

and the dissociation of bases to the equation

$$BH^+ + HS \rightleftarrows B + H_2S^+.$$

Shkodin and Sadovnichaya[77–81] measured K_{diss} for various bases by the electrical conductivity method and showed that anhydrous acetic acid increases the strength of all weak bases relative to water; one group of bases, with strengths close to that of the alkali metal acetates ($pK(H_2O) \simeq 4.3$–4.6) are levelled, and the other group of weaker bases ($pK(H_2O) > 5$) are differentiated. The bases are much weaker in propionic acid than in acetic acid. The strengths of bases which are very weak in water are increased in propionic acid, however. The differentiation of bases in propionic acid is much less than that in acetic acid. This confirms that in aliphatic acids the strength of electrolytes is inversely proportional to the magnitude of the dielectric constant.

Electrical conductivity data have been used to calculate p*K* for perchloric (2.85), hydrochloric (5.46), sulphuric (4.5), and hydrobromic (4.10) acids. The behaviour of acids and bases in a medium of acetic acid and its mixtures with other solvents has also been studied by a number of other workers[82–92].

Dulova and coworkers[93–99] studied the differentiating action of alcohols, esters, glycols, and ethylene chloride, and indicator and spectrophotometric methods were used to determine K_{diss} for a number of acids. The authors cited consider that the differentiating action of hydroxyl-containing solvents is related chiefly to the size of the radical and its three-dimensional structure.

A large number of determinations of K_{diss} for acids in methanol and ethanol and their mixtures with water have been made[100–122]. Sano[123,124] determined K_{diss} for a large number of acids in methanol and established that the values of K_{diss} decrease by a factor of approximately 80 000 relative to water. Tabagua[125–128] determined K_{diss} for a number of organic acids in methanol and ethanol and their mixtures with water, and showed that the values of K_{diss} for the acids decrease with increase in the concentration of alcohol in the mixture, and that at low concentrations of the alcohol the strength of the acids depends only on the dielectric constant of the medium. With increase in the alcohol concentration, the influence of the nature of the acids is observed, the changes in K_{diss} for weak acids being less marked than those for strong acids, due to the difference in the solvation energies of the ions and molecules.

Aleksandrov and coworkers[129] determined p*K* for a number of acids in methanol and its mixtures with water and benzene. Izmailov and Spivak[130] determined pK_{rel} for a number of acids in aprotic solvents. Data have been published on the dissociation of electrolytes of the acid–base type in formic acid[131,132], formamide[133–136], dimethylformamide[137], mixtures of dioxan and water[138–145], and other solvents[146–159]. A simple and rapid method for estimating solvent influence on the strengths of acids and bases involves the determination of the relative acidic or basic strength of electrolytes from the half-neutralisation potentials ($E^{1/2}$). When 50% of the weak acid or weak base is neutralised, pH = p*K*, so that $E^{1/2}$ can characterise the relative strength of electrolytes in non-aqueous solutions. Values of $E^{1/2}$ for derivatives of benzoic acid have been determined in pyridine, acetonitrile, methyl isobutyl ketone, 2-nitropropane, *o*-nitrotoluene, nitrobenzene, dimethylformamide, chlorobenzene, and bromobenzene[160]. A linear dependence of $E^{1/2}$ on $pK(H_2O)$ was obtained for all solvents. The solvents studied exhibit a strong differentiating action, and in these solvents it is possible to analyse a mixture of two acids with $\Delta pK(H_2O) = 0.94$. Determination of $E^{1/2}$ for derivatives of phenylurea in n-butylamine showed that the phenyl- and chlorophenyl-derivatives exhibit more strongly acidic properties in n-butylamine than urea and its alkyl derivatives[161].

The dependence of the half-neutralisation potentials on the values of $pK(H_2O)$ for electrolytes gives information on the differentiating action of non-aqueous solvents. The differentiating action of solvents is characterised by the slope of the straight line, which is determined by the number of mV per unit of $pK(H_2O)$. The steeper the straight line, the stronger the differentiating action shown by the solvent with respect to a given group of electrolytes. Comparison of the differentiating properties of nine non-aqueous solvents by measurement of the values of $E^{1/2}$ for the nitro- and halogeno-derivatives of phenol was carried out by Crabb and Critchfield[162]. They arranged the solvents studied in the following order of decreasing differentiating action: t-butyl alcohol > pyridine > tetrahydrofuran > > isopropyl alcohol > dimethyl sulphoxide > acetone > > acetonitrile > ethylene glycol > water. For derivatives of picric acid, the values of $E^{1/2}$, measured in acetone, were found to be linearly dependent on $pK(H_2O)$.[163]

We made a quantitative estimate of the differentiating action of alcohols, ketones, hydrocarbons, and mixed solvents with respect to monobasic aromatic acids, dicarboxy-

lic acids, and organic bases[1]. The observed dependence of $E^{1/2}$ on $pK(H_2O)$ showed that the strongest differentiating action with respect to monobasic aromatic acids is shown by ethyl methyl ketone, with respect to dicarboxylic acids by isopropyl alcohol and ethyl methyl ketone, and with respect to organic bases by mixed solvents: benzene or chloroform with ethyl methyl ketone or acetonitrile.

Measurement of the relative basic strength of phosphines in nitromethane showed that in the phosphine series the strongest electrolytes are tertiary phosphines, whereas in the amine series the strongest electrolytes are primary amines[164]. A linear dependence of $E^{1/2}$ on $pK(H_2O)$ was observed for derivatives of phenothiazine and sympathomimetic amines in acetone, acetonitrile, acetic acid, isopropyl alcohol, and nitromethane[165]. A common linear relationship was observed for all bases in a medium of acetic acid. In acetone, acetonitrile, and nitromethane, which exhibit effective differentiating properties, a characteristic relationship was observed for each group of bases. Isopropyl alcohol has a levelling action on amines. The dependence of $E^{1/2}$ on $pK(H_2O)$ makes it possible to estimate $pK(H_2O)$ for acids and bases for which these values have not previously been determined experimentally[1,89].

An important characteristic of a solvent, determining its scale of acidity in titrations, is the autoprotolysis constant (K_S). A number of authors have determined the values of K_S for acetic acid[166], acetic anhydride[167], ethanol, n-propanol, isopropyl alcohol[168,169], monoethanolamine[170,171], ethylene glycol and propylene glycol[76], dimethylformamide[172], dimethyl sulphoxide[74], and acetonitrile[66].

A number of studies have been devoted to the determination and use of Lewis acids in titrations in non-aqueous solvents[173-186].

Thus a survey of the theory of the analytical chemistry of non-aqueous solutions shows an increase in the number of papers devoted to the study of acid–base reactions in non-aqueous solutions. These studies, however, do not include such solvents as ketones, nitro-derivatives of hydrocarbons, and various mixed solvents, which have found extensive practical application as differentiating solvents. It is necessary to extend studies on the quantitative estimation of the influence of solvents on the dissociation of electrolytes, together with measurements of K_{diss}. Estimation of the relative strengths of electrolytes from half-neutralisation potentials gives extremely valuable information for the development of new methods for the analysis of mixtures of electrolytes. It is also necessary to extend studies on the determination of the autoprotolysis constants of non-aqueous solvents.

III. PRINCIPLES OF THE ACID–BASE TITRATION OF NON-AQUEOUS SOLUTIONS

In the selection of a method for the titration of acids, bases, and salts in non-aqueous solutions, particularly in the selection of a method for the differentiated analysis of mixtures of electrolytes, it is necessary to have a theoretical basis for the selection of the medium for the titration (solvent), the standard solution of the reagent (titrant), and the method for determining the equivalence point. Only a coordinated selection of these titration conditions permits a more rational and effective method for the differentiated determination of the individual compounds in multi-component mixtures[5,187].

1. Solvents used for Acid–Base Titration

In the determination of compounds which exhibit acid–base properties in non-aqueous solutions, various classes of organic solvent can be used as media for the titration: organic acids (formic, acetic, etc.), amines and heterocyclic bases (butylamine, ethylenediamine, pyridine, piperidine, etc.), glycols, alcohols (methaol, ethanol, propanol, isopropyl alcohol, etc.), ketones (acetone, ethyl methyl ketone, methyl isobutyl ketone, etc.), nitriles (acetonitrile), amides (dimethylformamide, formamide, etc.), esters and ethers (diethyl ether, dioxan, esters of acetic acid, etc.), hydrocarbons and their halogeno- and nitro-derivatives (benzene, chloroform, carbon tetrachloride, nitromethane, nitrobenzene, etc.), and various mixtures of these solvents.

In the last 4–5 years, a number of new organic solvents exhibiting valuable properties have been introduced into analytical practice, for example t-butyl alcohol, dimethyl sulphoxide, tetramethylguanidine, and various mixed solvents (mixtures of aprotic solvents with ketones and nitriles). t-Butyl alcohol[162,188-190] has proved to one of the best solvents for the titration of very weak acids; it has a lower acidity than the lower alcohols, and its acid solutions have a high stability. The differentiated titration of mixtures of various inorganic and organic acids can be carried out in t-butyl alcohol.

Dimethyl sulphoxide is an effective solvent for many organic compounds[162,191-194], and unlike a number of solvents it is not toxic and has no odour. The presence of the semipolar bond between sulphur and oxygen in dimethyl sulphoxide gives it protophilic character and leads to an increase in the strength of weak organic acids dissolved in it. This solvent is characterised by a fairly large acidity scale ($pK = 18$) and high dielectric constant (40), and exhibits the same differentiating properties as dimethylformamide, but it does not contain acidic and basic impurities, and therefore does not require preliminary purification. Strong and weak organic acids can be titrated in dimethyl sulphoxide, and the titration of phenols is particularly effective (phenol, guaiacol, eugenol, etc.)[191]. Williams and coworkers[195,196] studied the properties of tetramethylguanidine and suggested its use as solvent without preliminary purification for the potentiometric and visual titration of phenols.

Solvents used for the titration of bases. Compounds which exhibit basic properties in non-aqueous solutions can be determined by titration in protolytic (protogenic and amphiprotic), aprotic, and various mixed solvents.

Among the protogenic solvents for the determination of weak bases, extensive use is still made of anhydrous acetic acid[197-243], first proposed for this purpose by Conant and Hall[8]. In acetic acid, the strengths of bases with $pK(H_2O) = 10-14$ increase, but do not reach the value 4.3, and the bases exhibit their own individual properties. Thus it has been possible to carry out the differentiated titration of two-, three-, and four-component mixtures of bases in acetic acid[244-247].

Bases can be titrated in mixtures of acetic acid and acetic anhydride[248,249], or in pure acetic anhydride[220,250-256]. Acetic anhydride has found application as differentiating solvent for the differentiated titration of amines, sulphoxides, and amides[257]. The improvement in the conditions for the titration of bases in acetic anhydride compared with acetic acid may be attributed to its higher dielectric constant.

Unlike acetic acid, acetic anhydride differentiates bases over the entire scale of acidity[89]. The addition of hydrocarbons, their halogeno-derivatives, dioxan, or ketones to acetic acid or to acetic anhydride makes the end point of the titration sharper, due to a decrease in the ionic product of the medium[205,222,223,249,251,258-261]. The use of mixtures of formic acid with acetic anhydride[262] and propionic acid[263] as media for the titration of bases has also been described.

Of the amphiprotic solvents for the titration of bases, most extensive use has been made of alcohols, ketones, and nitriles. In the titration of bases in alcohols, the end points of the titrations are insufficiently sharp. Alcohols do not exhibit strong differentiating properties with respect to bases[244,264-267]. For the differentiated titration of mixtures of bases, extensive use is made of ketones, particularly acetone[208,233,268-270], ethyl methyl ketone[244,267,271-275], and isobutyl methyl ketone[268,276]. The differentiated titration of two-, three-, and four-component mixtures of strong and weak bases has been carried out in ethyl methyl ketone[267,271,275,277].

Acetonitrile has found extensive application as medium for the titration of bases; this solvent is used for the titration of individual bases[208,224] and for the differentiated titration of their mixtures[233,278]. The end points of the titration of bases in ketones and acetonitrile are sharper than those in protogenic solvents and alcohols, apparently due to the low values of the ionic products of these solvents.

Strong differentiating properties with respect to weak bases are also shown by nitrobenzene and nitromethane. In nitrobenzene it is possible to carry out the differentiated titration of various mixtures of bases whose $pK(H_2O)$ values differ by unity, and in nitromethane it is possible to carry out the differentiated titration of mixtures of components whose pK values differ by 0.3 unit[278]. The conditions of the titration in nitrobenzene are improved considerably when acidic solvents are added[279-281]. Study of the influence of the addition of organic acids on the titration of a mixture of diethylaniline and *m*-nitroaniline in nitrobenzene showed that the addition of 11.1% of a mixture of acetic and formic acids (1 : 3) increases the differentiating properties of the nitrobenzene[279].

Aprotic solvents used for the titration of bases include hydrocarbons (benzene, chlorobenzene, chloroform, dichloroethane, etc.)[268,282-292]. In titrations in aprotic solvents of low dielectric constant values (2–5), alcohols, ketones, and nitriles are added in proportions from 10 : 1 to 4 : 1, to increase the dielectric constant of the solution[267,293-296]. The end point of the titration is less sharp when alcohols are added than when ketones and nitriles are added[267]. Many diamines can be titrated as diacid bases in mixed solvents consisting of mixtures of chloroform or benzene with ethyl methyl ketone or acetonitrile (4 : 1)[267,294-296]. The production of the second inflection in the titration is due to the precipitation of the normal salt of the diamine and perchloric acid, sparingly soluble in aprotic solvents.

Bases can also be titrated in mixed solvents such as *m*-cresol + acetonitrile (1 : 1)[297], dioxan + chloroform[234], and dioxan + acetic acid + nitromethane (75 : 5 : 20)[298]. The titration of compounds with basic properties can also be carried out in acetonitrile[299,300], dimethyl sulphoxide[194], pyridine[301], ethyl acetate[302], and methylcellosolve[303]. New methods have been described for the purification and control of the purity of various non-aqueous solvents[304-309].

Solvents used for the titration of acids. The determination of compounds which exhibit acidic properties in non-aqueous solutions can be carried out by titration in aprotic and protolytic (protophilic, protogenic, and amphiprotic) solvents. The most widely used aprotic solvents are chloroform[310,311] and benzene[312,314]. In aprotic solvents, because of the low dielectric constant, it is possible to titrate not only individual strong, weak, and very weak acids, but also mixtures of acids differentially. Alcohols[190,315,316], ketones[317], and acetonitrile[318,319] in proportions from 3 : 1 to 10 : 1 are often used to increase the dielectric constant of the solution.

Amphiprotic solvents used for the same purpose include various alcohols, ketones, nitriles, esters, and other solvents. Alcohols, as the most readily available and inexpensive solvents, are widely used for the titration of strong and weak acids. Thus methanol[311,320,321], ethanol[311,321-325], propanol and isopropyl alcohol[162,311,326-328], butanol, isobutyl alcohol, and t-butyl alcohol[162,188,189,311], and mixtures of alcohols with one another[329] or with benzene[190,315,316], dioxan[324], pyridine[330], and ketones[331,332] can be used for the titration of higher aliphatic acids, dicarboxylic and inorganic acids, nitrophenols, and other compounds. Co-solvents are used to increase the solvent power of the alcohol and to obtain sharper end points in the titration. Mixtures of inorganic acids are readily titrated in alcohols, particularly lower alcohols (methanol and ethanol)[1]. Mixtures of carboxylic acids with phenols and mixtures of dicarboxylic acids are titrated in less acidic alcohols, such as isopropyl alcohol, isobutyl alcohol, and t-butyl alcohol[188,318,333].

Ketones are the best solvents for the titration of acids. Inorganic and organic acids, phenols, and a number of other substances can be titrated in acetone[193,310,311,332-348], ethyl methyl ketone[310-313,332-334,347,349-354], butyl methyl ketone and isobutyl methyl ketone[193,347] and mixtures of ketones with water[350,355,356], alcohol[331,332], dimethylformamide[350], and acetonitrile[318]. Ketones, because of their amphoteric character, low dielectric constants, and low K_S values, are excellent differentiating solvents. Ketones can be used successfully not only for the titration of two-, three-, and four-component mixtures of various acids, but also for the titration of five- and six-component mixtures of strong, weak, and very weak acids[311,333,353,354]. Nitriles[162,193,310-311,333,347,357] and esters of acetic acid[310,311,333] are effective differentiating solvents. Mineral and organic acids and their mixtures can be readily titrated in these media. High-frequency and potentiometric methods have been used for the titration of acids and their mixtures in dioxan and its mixtures with water[193,358-361].

Protophilic solvents are used as media for the titration of very weak acids. Phenols and weak carboxylic acids can be successfully titrated in ethylenediamine[193,362-366] and butylamine[161,316,363]. The titration of strong, weak, and very weak acids is carried out in pyridine[162,193,314,330,336,337,347,358,363,365,367-369] and piperidine[193,363]. Because of its low dielectric constant (12.5), pyridine is an effective differentiating solvent for the titration of mixtures of strong, weak, and very weak acids. In addition to amines, various amides can be used as media for the titration of acids. Various derivatives of phenols, carboxylic acids, and mineral acids can be effectively titrated in dimethylformamide[172,193,314,332,347,362,363,365,370-374], but the presence of water greatly distorts the results of the titration. Dimethylformamide exhibits weak basic properties, so that it can be used for the differentiated titration of mixtures of acids[347,371,375].

Protogenic solvents used for the titration of mineral acids include anhydrous formic and acetic acids[376-379]. In acetic acid, which has a low dielectric constant, it is possible to titrate differentially mixtures of inorganic acids

with one another and with organic acids[376-378]. Glycol solvents (mixtures of glycols with alcohols, ketones, hydrocarbons, and their halogeno-derivatives)[162,380-382] exhibit weak acidic properties. Mineral and organic acids and their mixtures can be determined in glycol solvents. Tetrahydrofuran[162,193,383], methylene chloride[382,384,386], acetyl chloride[386], and derivatives of aryl amides[387] are used successfully as solvents for the determination of individual carboxylic acids and their mixtures.

2. Titrants used for the Titration of Non-aqueous Solutions

Acidic titrants. The most widely used titrants for the titration of non-aqueous solutions of compounds of basic character are solutions of perchloric acid in acetic acid[198-200, 202-204,225-228,230-234,243-246], dioxan[204,210,241,251,255,257,259,266, 278,286-288,298,388], ethyl methyl ketone[267,273-275,277,294], mixtures of acetic acid and acetic anhydride (1 : 1)[389,390], ethanol[391], methylcellosolve[303], mixtures of acetonitrile and *m*-cresol[297], etc. The differentiated titration of mixtures of diamines, which can be titrated in a medium of benzene or chloroform with acetonitrile (4:1), has been carried out using solutions of $HClO_4$ in the same solvents[267,296]. The use of these titrants gives titration curves with sharper inflections than those obtained when a solution of $HClO_4$ in ethyl methyl ketone is used.

Various workers have used solutions of HCl in isopropyl alcohol[265] and isobutyl methyl ketone[276] for the determination of bases. Bases have been titrated with sulphonic acids, for example *p*-toluene-sulphonic acid in a mixture of ethanol and isopropyl alcohol (1 : 1) or in a mixture of chloroform with 1% ethanol, dioxan, and other solvents[268, 284,285,290,392], and also fluorosulphonic acid[393-396], trifluoromethyl sulphonic acid[397], and chlorosulphonic acid[398]. In a medium of acetic acid, fluorosulphonic acid is stronger than perchloric acid, and the stability of its solutions and the ease of preparation give grounds for considering it a better titrant than perchloric acid[393]. Study of the behaviour of standard methanol, ethanol, and mixed (glycol–methanol, glycol–isopropyl alcohol, and acetone–chloroform) solutions of fluorosulphonic acid[396] has shown that best results are achieved in the titration of bases with a methanol solution of fluorosulphonic acid.

Bases are also titrated with picric acid[399], trichloroacetic acid[392], acetic anhydride perchlorate[400], and an acetic acid solution of sulphur trioxide[401].

Solutions of $HClO_4$ in glacial acetic acid are standardised using tri(hydroxymethyl)methylamine[402]. An advantage of this reagent compared with potassium hydrogen phthalate is that it dissolves in acetic acid without heating, but it is a weaker base than potassium hydrogen phthalate and diphenylguanidine. $HClO_4$ solutions are also standardised using hexamethylenetetramine and pyramidone[241], and *p*-toluenesulphonic acid is standardised using strychnine[284].

Basic titrants. Methanol[320,321,343,345], ethanol[323, 331,335,340,341,375,384], isopropyl alcohol[380], and mixed[403] standard solutions of potassium hydroxide and sodium hydroxide are most widely used as titrants for the titration of compounds of acidic character in non-aqueous media. Extensive use is also made of alcoholic and mixed solutions of alkali metal alkoxides—sodium, potassium, and lithium methoxides[314,316,324,332,337,362,365,371,404] and isopropoxides[326]—and sodium aminoethoxide in ethylenediamine[366]. Organic bases used as titrants include triethanolamine[382], cyclohexylamine[383], diphenylguanidine[360,361], pyridine[377], and piperidine[381].

The strongest basic titrants in organic solvents are the quaternary ammonium hydroxides—tetramethylammonium[322,328], tetraethylammonium[310,312,334,344,347,349-354], and tetrabutylammonium[161,188-190,193,336,352,367,369,387,405,406] hydroxides—and various other derivatives of quaternary ammonium hydroxides, for example hexadecyltrimethylammonium[196], dodecyltrimethylammonium[327], and tributylethylammonium[368] hydroxides. Study of the properties of various derivatives of quaternary ammonium hydroxides, the factors influencing the stability of non-aqueous solutions of quaternary ammonium titrants[407], and the influence of the structure of the quaternary ammonium cation on the titration of various acids[408] by Harlow established that tetramethylammonium, tetrabutylammonium, and tetraethylammonium hydroxides are the most stable titrants, and trimethylbenzylammonium hydroxide the least stable.

In connection with the continuous extension of the range of application of quaternary ammonium bases, several new methods have been proposed for preparing solutions of these compounds. Harlow and Wyld[409] proposed a rapid and convenient method for preparing solutions of quaternary ammonium hydroxides, based on the reaction between potassium hydroxide and the quaternary ammonium chlorides in isopropyl alcohol. Gur'ev[410] used mercuric oxide in place of silver oxide for the preparation of solutions of tetramethylammonium and tetraethylammonium hydroxides. Kreshkov and coworkers[411] developed a very convenient method for preparing solutions of quaternary ammonium hydroxides by ion exchange; the titrants obtained by this method are highly pure.

3. Methods for Determining the Equivalence Point

Visual and physicochemical methods for determining the equivalence point are widely used in titrations in non-aqueous solutions. The potentiometric method[26,412-420] is the most widely used method of titration in non-aqueous solutions. The indicator electrodes used in the potentiometric titration include the hydrogen[413], glass[413,416], graphite[415], platinum[316], platinum oxide[417], antimony[418,421], and silver chloride[419] electrodes. A comparative study has been made of various electrode systems for titrations in acetic acid and dimethylformamide[420]. Comparison of platinum oxide and glass electrodes for acid–base titration in alcohols, ketones, acetonitrile, dimethylformamide, and mixed solvents[417] showed that the inflections observed are greater for the platinum oxide electrode than for the glass electrode.

A method for potentiometric titration at constant current strength[297], a dead-stop method[389], and a chronopotentiometric method which does not involve the use of a burette[422] have been described. Conductometric[25,423], high-frequency[25,27,87,424], and spectrophotometric[245,425] methods are widely used for titrations in non-aqueous media. Chronoconductometric titration in aqueous alcohol[426], thermometric titration in acetonitrile[357], acetic acid[427], and acetone[428], and coulometric[429], luminometric[430], dielectrometric[292], and amperometric[431,432] titrations have also been described. A number of papers have been devoted to the study of acid–base indicators for titrations in non-aqueous solutions[433-444].

IV. TITRATION IN NON-AQUEOUS SOLUTIONS OF BASES

1. Titration of Individual Compounds

Non-aqueous solvents can be used for the determination of the great majority of individual compounds which exhibit basic properties in non-aqueous solutions[1-5]. These compounds include aliphatic, aromatic, and heterocyclic amines[199,206,208,220-222,241,261,281,284,287,290,297,390,445], diamines[233,267,294-296,446], amides[230,250,251], imides[207], amine oxides, phosphine oxides, and aromatic *N*-oxides[255,447], compounds containing the mercapto-group[448], sulphonamides[449], pyrazolones[225,450], vitamins[204], antihistamines[205,223], antibiotics[259], alkaloids[226,228,229,234,249,285,292,293], and other compounds[198,200,224,232,234,240,256,258,286,288,289,451,452].

Shkodin and Karkuzaki[421] titrated very weak bases ($pK(H_2O) > 12$) such as urea, thiourea, caffeine, theobromine, etc. in a medium of absolute anhydrous acetic acid and its mixtures with acetic anhydride. They showed that the titration of these compounds becomes impossible when even small quantities of water are present.

Potentiometric titration at constant current strength in a medium of *m*-cresol–acetonitrile (1 : 1) has been used for the titration of monoacid and diacid aliphatic and aromatic amines and their nitro-derivatives[297], and methods have been described for the micro-titration of weak bases of $pK(H_2O) = 11$ (piperidine, benzidine, diphenylguanidine, pyridine, quinine, strychnine, etc.) in a medium of chloroform[284], dichloromethane, and chlorobenzene[290] with a solution of *p*-toluenesulphonic acid in a chloroform + ethanol medium.

In a 2 M benzene solution of nitrobenzene, modified by means of organic acids such as formic, acetic, or trichloroacetic, bases which are very weak in water (aniline, *p*- and *m*-chloroanilines, diethylaniline, *o*-, *m*-, and *p*-nitroanilines, and diphenylamine) behave as strong, intermediate, or weak bases, depending on the acid added[281].

Study of the possibility of titrating the amides of acids and various other weakly basic compounds (acetanilide and its derivatives) in a medium of acetic anhydride and its mixtures with acetone and chloroform (1 : 1)[251] has shown that the presence of electron-donating groups increases the basic strength and gives a sharper inflection in the titration. Alkaloids can be titrated in a mixture of acetic acid with acetic anhydride and other solvents. Mercuric acetate is added to the solvent to give a sharper inflection in the titration of alkaloids[249]. The conductometric titration of aldehydes and ketones as bases in a medium of H_2SO_4 with tetra(hydrogen sulphato)boric acid is possible[453].

When the compounds to be determined do not exhibit basic properties in non-aqueous solutions, they are treated beforehand with various reagents which convert them into basic compounds[233,237,252]. Thus carbonyl compounds react with various salts of hydroxylamine or hydrazine derivatives to form oximes or phenylhydrazones, which exhibit the properties of weak bases in a medium of acetic anhydride[237,252]. Diamines are oxidised with chloranil, and diimines are reduced with hydroquinone to form basic compounds which can be determined by titration[233]. A method has been described for the determination of acetic anhydride in acetylating mixtures, based on its reaction with aniline, excess of which is titrated in a medium of diethylene glycol[454].

2. Titration of Primary, Secondary, and Tertiary Amines

Mixtures of primary, secondary, and tertiary amines are still analysed by acetylation of the primary and secondary amines with acetic anhydride[201,235,303] and binding of the primary amines with salicylaldehyde[210,264,269,298,455] or phthalic anhydride[202,456].

Strepikheev and coworkers[269] determined primary, secondary, and tertiary amino-groups in polynuclear polyamines in an acetone + acetic acid medium, using salicylaldehyde to bind the primary amines. The authors cited[269] showed that phthalic anhydride combines not only with primary but also with secondary amino-groups. Other workers also established that when solutions of primary and secondary amines with a high concentration of secondary amines are boiled for a prolonged period, the phthalic anhydride reacts to form neutral compounds. In order to hydrolyse the products, the reaction is carried out in 98% acetic acid or in the presence of perchloric acid[202]. Pyromellitic anhydride in a medium of dimethyl sulphoxide has been used to bind primary and secondary amines[194]. The reaction is more rapid when this acetylating reagent is used. A method has been proposed for the determination of primary, secondary, and tertiary amines, based on the difference in the rates of formation of thiourea by the reaction of the amines with isothiocyanates in acetic acid. Samples are removed at measured time intervals and the unreacted amine is titrated[236].

A method has been developed for the determination of tertiary amines in the presence of primary and secondary amines, based on the binding of the primary and secondary amines in the form of thiourea derivatives by the reaction with phenyl isothiocyanate followed by titration of the tertiary amine in isobutyl methyl ketone. This method is not applicable, however, when the secondary amines are N-secondary alkylanilines or ortho-substituted *N*-alkylanilines, where there is steric hindrance to the reaction with phenyl isothiocyanate[276]. In the determination of amine oxides and tertiary amines in the presence of one another, the latter are bound with alkyl halides, which convert them into neutral quaternary ammonium salts[265].

In the quantitative analysis of mixtures of higher aliphatic amines in the products of the hydrogenation of the nitriles of the higher carboxylic acids, the primary amines are bound with acetylacetone and the secondary amines are titrated acidimetrically; the sum of the primary and secondary amines is determined by titration after the amines have been converted into the dithiocarbamic acids[457]. Chloroform and methanol are used as solvents.

To determine piperazine, hydroxyethylpiperazine, and dihydroxyethylpiperazine in the presence of one another, the first two components of the mixture are separated from the dihydroxyethylpiperazine by precipitation with carbon disulphide from a solution of the mixture in chloroform[299], and the dihydroxyethylpiperazine is titrated. The precipitate is dissolved in acetonitrile, and the hydroxyethylpiperazine is determined by titration, after acetylation.

In the titration of amines by a solution of *p*-toluenesulphonic acid using the dielectrometric method, it was found that the titration curves for primary and secondary amines differ from those for tertiary amines[392]. This feature was used for the differentiated titration of a mixture of primary, secondary, and tertiary amines. The determination of tertiary amines in the presence of n-octanol[227] and of primary aliphatic amines in the presence of secondary and tertiary amines by photometric titration with a solution of

2-ethylhexanal[458], and also a method for determining primary and secondary diamines in a medium of ketones[459], have been described.

3. The Differentiated Titration of Mixtures of Bases

Methods which make possible the separate determination of each component in complex mixtures of bases with very similar $pK(H_2O)$ values are of particular interest. Two-, three-, and four-component mixtures of bases have been titrated, for example tetraethylammonium hydroxide + n-butylamine + diethylaniline, piperidine + 1,10-phenanthroline, piperidine + benzimidazole + methylbenzimidazole, etc. in ethyl methyl ketone[271,275-277], quinoline + aniline in acetonitrile, nitrobenzene, and nitromethane[278], diethylaniline + aniline or *m*-nitroaniline in a benzene solution of nitrobenzene, modified with acetic and formic acids[279-281], mixtures of amines, sulphoxides, and amides, and mixtures of pharmaceutical products in acetic anhydride[89,257], and mixtures of diamines in mixed solvents consisting of an aprotic solvent and an amphiprotic solvent[267,294-296]. Mixtures of weak bases are also titrated in acetic acid[233,244-247] and other solvents[260,262].

A method has been developed for the analysis of two-, three-, and four-component mixtures of aliphatic, aromatic, or heterocyclic amines, sulphoxides, and amides of carboxylic acids by titration in a medium of acetic anhydride. In the titration of four-component mixtures the first inflection in the titration corresponds to the neutralisation of the aliphatic amine, the second to the aromatic amine, the third to the sulphoxides, and the fourth to the amides[257]. The differentiated titration of a mixture of weak bases with $pK(H_2O) = 10-14$ (amidopyrine + antipyrine, caffeine + phenacetin, etc.) has been carried out in acetic anhydride[89].

We developed a method for the analysis of two- and three-component mixtures of diamines and of monoamines with diamines in mixed solvents—chloroform or benzene with ethyl methyl ketone or acetonitrile (4 : 1)[267,294-296]. The method can be used to analyse two-component mixtures of the *p*- and *o*- and *p*- and *m*-isomers of phenylenediamine, hexamethylenediamine + *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine + *p*-phenylenediamine, tyramine + *o*- + *m*-phenylenediamines, and a number of other mixtures.

Kreshkov and Vasil'ev[244,245] developed a method for the spectrophotometric titration of three- and four-component mixtures of weak and very weak bases ($pK(H_2O) > 13.5$) in a medium of acetic acid. Titration of *o*-nitroaniline + 4-methyl-2-nitroaniline + *p*-bromoaniline, *o*-nitroaniline + *m*-nitroaniline + 4-methyl-2-nitroaniline + *p*-nitrosodimethylaniline, and other mixtures showed that the spectrophotometric method can be used to analyse mixtures with a difference in $pK(H_2O)$ values of 0.8–1.5. Mixtures of the isomers of nitro-*o*-toluidine and nitro-*p*-toluidine, nitroaniline and nitro-*o*-anisidine have been titrated in a medium of acetic acid and its mixtures with acetone (1 : 4)[260]. Two-, three-, and four-component mixtures of weak bases with $pK(H_2O) = 10-13.81$ have been titrated in acetic acid by a conductometric method[78,247].

Lorenz and Parks[233] showed that it is possible to analyse mixtures of *NN'*-diaryl-*p*-phenylenediamines and *NN'*-diaryl-*p*-phenylenediimines in a medium of acetic acid. Chloranil was added when the mixture contained an excess of *NN'*-diaryl-*p*-phenylenediamine, and hydroquinone was added when the mixture contained an excess of *NN'*-diaryl-*p*-phenylenediimine. The analysis of mixtures of acylamidines, such as *N*-benzoylbenzamidine, *N*-thiobenzoylbenzamidine, dibenzamide, etc.[460]

V. TITRATION IN NON-AQUEOUS SOLUTIONS OF ACIDS

All organic and inorganic compounds which exhibit acidic properties can be determined in non-aqueous solvents. These compounds include phenols, mono-, di-, and tri-basic aliphatic and aromatic carboxylic acids, and also mono- and di-basic inorganic acids, acid anhydrides and chlorides, enols, imides, amides, and other compounds such as esters and alcohols[1-5].

1. Titration of Compounds Exhibiting Weakly Acidic Properties

Enols and their derivatives are successfully titrated by the potentiometric method in tetramethylguanidine[195,196], dimethyl sulphoxide[74,75,191], t-butyl alcohol[162,188,189,405], and *NN*-dimethylarylamides[387]. A number of papers have been devoted to the titration of phenols in ethylenediamine[362,364], dimethylformamide[172,362,370,372], acetone[347], ethyl methyl ketone[347,349], alcohols[188,328], and other solvents[331,347]. Phenols, cresols, and their derivatives are determined by high-frequency, conductometric[190,339,345,363], and spectrophotometric[329] methods. Polycyclic phenolic compounds are titrated in a medium of pyridine and acetone[337], substituted phenylureas in a medium of butylamine[161], and acylamidines in a medium of pyridine[367]. The differentiated titration of phenol and its nitro-derivatives has been carried out in ethyl methyl ketone[333] and in other solvents[347] by a potentiometric method, and mixtures of isomers of cresol and xylenone[339,345] have been titrated in a medium of acetone by a high-frequency method.

A number of ethers and esters have been titrated in non-aqueous solvents. Pathochornik and coworkers[324] established that in an ethanol + dioxan mixture, esters of *p*-nitrophenol and esters of thiophenol behave as acids and can be titrated with CH_3ONa solution. A method has been developed for the analysis of diethyl malonate and its derivatives, based on enolisation and subsequent titration of the resulting acid in a medium of ethylenediamine, dimethylformamide, or pyridine[365]. The titration of *p*-nitrophenylhydrazones of aldehydes, ketones, and hydrocarbons as acids in a medium of pyridine with tetrabutylammonium hydroxide solution has been studied. The nitrophenylhydrazones of dicarbonyl compounds can be titrated as dibasic acids[369].

Harlow[461] published an interesting study of the influence of potassium ions on the shape of the potentiometric titration curves for weak acids in pyridine. The presence of 10% potassium ions in the solution being titrated decreases considerably the magnitude of the potential jump at the equivalence point.

2. Titration of Monocarboxylic Acids.

Aliphatic and aromatic carboxylic acids and their hydroxo-, halogeno-, nitro-, and other derivatives can be successfully titrated in non-aqueous solvents[366,406,462]. Of particular importance is the titration of the water-insoluble

higher aliphatic acids[315,342,463], benzoic acid and its derivatives, α- and β-naphthalenecarboxylic acids and their derivatives, and a number of other acids[335,352,361]. All carboxylic acids can be titrated with sufficient accuracy in alcohols[342], ketones[193,332,338,342], chloroform[333], ethylenediamine[366], mixtures of dioxan and water[359,360], and a number of other solvents[315].

In differentiating solvents it is possible to titrate mixtures of benzoic and salicylic acids, and also the *o*- and *m*-, and *o*- and *p*-isomers of hydroxybenzoic acid[333]. The differentiated titration of mixtures of naphthalenecarboxylic acids and their hydroxy-derivatives[352] and naphthols[331] can be carried out in a medium of ketones. The differentiated titration of four-component mixtures of carboxylic acids and phenols can be carried out in t-butyl alcohol[188]. Vasil'ev and Tumovkii[212] have titrated two-component mixtures of amphoteric compounds: 1-naphthylamine + 4-nitro-1-naphthylamine, 4-aminophenol + 2-nitro-4-aminophenol, etc., as acids with sodium methoxide in a medium of acetone + methanol (2 : 1) and as bases with perchloric acid in a medium of acetic acid.

3. Titration of Dicarboxylic Acids

In connection with the vast technical importance of dicarboxylic acids, which are widely used in the production of plastics, paints, synthetic fibres, and other macromolecular products, a large number of papers have recently been published on the titration of dicarboxylic acids and their mixtures in non-aqueous solvents[318,335,349,350,464,465]. Non-aqueous solvents can be used as media for the titration of unsaturated dicarboxylic acids (maleic, fumaric, itaconic, and citraconic), saturated dicarboxylic acids (from oxalic to sebacic), and aromatic dicarboxylic acids (the isomers of phthalic acid), and also for various mixtures of dicarboxylic acids, including mixtures of isomers (maleic and fumaric, itaconic and citraconic), and mixtures of acids of the same homologous series (oxalic and succinic, sebacic and adipic). Dicarboxylic acids and their mixtures can be titrated by potentiometric[318] and high-frequency[374,466-468] methods.

The differentiated titration of mixtures of dicarboxylic acids can be carried out in isopropyl alcohol, acetone, ethyl methyl ketone, acetonitrile, and mixtures of aprotic solvents with alcohols, ketones, and acetonitrile[469-472]. For example, a mixture of maleic and phthalic acids can be titrated in ethyl methyl ketone, a mixture of maleic and fumaric acids can be titrated in acetonitrile, and a mixture of sebacic and azelaic acids can be titrated in a chloroform + acetonitrile (4 : 1) mixture.

We developed methods for the quantitative differentiated titration of aromatic dicarboxylic acids, for example mixtures of iso- and terephthalic acids[469], mixtures of phthalic, isophthalic, and terephthalic acids, etc.[470] For the determination of all three isomers, a method was proposed based on two parallel titrations of the mixtures of acids in ethyl methyl ketone, one specimen being titrated with $(C_2H_5)_4NOH$ solution, and the second with KOH solution. The curves obtained were used to calculate the concentration of each isomer in the mixture[351,470]. The method can also be used for the analysis of a three-component mixture of maleic, fumaric, and phthalic acids[318].

Methods have been developed for the titration of mixtures of dicarboxylic acids with one another[335] and with inorganic acids such as hydrochloric[318], nitric, etc.[343] in a medium of ketones.

4. Titration of Inorganic Acids

Non-aqueous solvents can be used as media for the rapid and sufficiently accurate determination of individual inorganic acids, for example phosphoric[377], nitric[188,321,377], sulphuric[188,355,377,382], perchloric[188,377,382], and others[188,377], and also for the differentiated titration of various acid mixtures. Thus mixtures of inorganic acids, for example sulphuric and perchloric[385], can be analysed by potentiometric titration in methylene chloride. Zarinskii and Gur'ev used a high-frequency method for the differentiated titration of mixtures of inorganic acids in acetic acid[378] and in glycol solvents[380]. The differentiated titration of two-component mixtures of inorganic acids, for example sulphuric and phosphoric, nitric and phosphoric, sulphuric and hydrochloric, etc. has been carried out by a conductometric method in ethanol[322] and in acetic acid[376]. Potentiometric titration can be used for the analysis of mixtures of inorganic and organic acids, for example hydrochloric and acetic acids in methylene chloride[384], sulphuric and phenolsulphonic acids in a dioxan + diethylene glycol mixture[381], sulphuric and sulphonic acids[344] and nitric and monochloroacetic acids[346] in acetone, and sulphuric and lactic acids in isopropyl alcohol[326].

Drozdov and Kolchina[473] developed a potentiometric method for the analysis of a three-component mixture of hydrochloric acid, methylphosphonic acid, and isobutyl hydrogen methylphosphonate, and also other mixtures of phosphoric acid derivatives of considerable practical importance.

We developed methods for the titration of two-, three-, four-, five-, and six-component mixtures of strong, weak, and very weak organic and inorganic acids in a medium of ketones and other differentiating solvents[310,353,354]. Methods have been proposed for the determination of mixtures of nitric acid with organic acids (nitrobenzoic acid, nitrophenols, and α-hydroxyisobutyric acid) in ethyl methyl ketone[334], and for the analysis of two- and three-component mixtures of nitric acid with monocarboxylic, dicarboxylic, and hydroxycarboxylic acids (nitric + adipic + oxalic) in methanol[320,321]. A method proposed for the analysis of mixtures of phosphoric and sulphuric acids, and of phosphoric and nitric acids in the presence of trioctylamine[1] is of considerable practical importance in phosphoric acid production.

5. Titration of Acid Anhydrides and Chlorides

A number of papers[313,330,474,475] have been devoted to the determination of the anhydrides and chlorides of carboxylic acids. The chlorides of aliphatic and aromatic carboxylic acids exhibit acidic properties in tetrahydrofuran and can be titrated with cyclohexylamine solution[383]. The method is suitable for the determination of all acid chlorides, including those containing readily hydrolysed groups, and also for the determination of aromatic compounds containing two acid chloride groups. A method has been proposed for the determination of an acid chloride in the presence of pyridine in a medium of dioxan; excess of water is removed with acetic anhydride, and the resulting pyridinium chloride is titrated with perchloric acid solution[358]. A method has been developed for the analysis of the actual concentration of the acid chlorides of carboxylic acids in mixtures with the acid and hydrochloric acid. The method is based on the titration of the acid chloride with sodium hydroxide in ethanol before and after heating, and can be used to

determine the concentrations of hydrochloric and carboxylic acids and the acid chloride[325].

Emelin and Svistunova have proposed a number of methods for the determination of the anhydrides and chlorides of carboxylic acids[341,348,356]. The determination of acetic anhydride in acetylating mixtures is based on the reaction with aniline, excess of which is titrated in diethylene glycol[454], and the determination of the chloride of isophthalic acid is based on the reaction of the chloride with aniline. The differentiated titration of the resulting anilinium chloride and isophthalic acid is carried out potentiometrically in a medium of acetone with alcoholic sodium hydroxide solution.

VI. TITRATION IN NON-AQUEOUS SOLUTIONS OF SALTS

The great majority of salts can be titrated in non-aqueous solvents, since many salts which are neutral substances in aqueous solution exhibit acidic or basic properties in non-aqueous solutions. Titration in non-aqueous solutions not only makes it possible to determine individual salts, but also to analyse multicomponent mixtures and mixtures of salts with acids or with bases[476].

1. Titration of Individual Salts

A number of salts exhibit acidic properties in protophilic and amphiprotic solvents and can be titrated as acids[476]. For example, inorganic salts such as the fluorides of multivalent metals (Mo, Ta, Ti, Nb, and W) can be successfully titrated in a mixed ethyl methyl ketone + benzene (1 : 1) solvent[317]; nitrates, bromides, and chlorides of the rare earth elements can be titrated in a medium of acetone + methanol (1 : 1); and lithium and sodium perchlorates can be titrated in pyridine[368]. Salts of organic acids can be titrated, for example zinc stearate in ethanol[323], and zinc styphnate in ethylenediamine[477]. Jasinski and coworkers titrated salts of organic bases, for example amine picrates in pyridine[403] and aromatic amine hexachlorotellurites in acetonitrile and dimethylformamide[478]. Salts of organic bases and mineral acids are readily titrated in methanol[1].

A number of salts exhibit basic properties in protogenic and amphiprotic solvents and can be titrated as bases[479-483,496-498]. Inorganic salts can be titrated, for example chlorides[484] in dioxan, nitrites in the presence of nitrates in ethyl methyl ketone[476], nitrates[485] and sulphates[486] in an acetic acid + acetic anhydride mixture, ammonium carbonate[487] in acetone, and salts of the rare earth elements in acetic acid, ethyl methyl ketone, and mixtures of glycol with alcohols[488,489].

Most salts of monobasic organic acids (the acetates, formates, benzoates, salicylates, lactates, etc. of lithium, sodium, calcium, zinc, cobalt, manganese, and other alkali and alkaline earth metals) can be successfully titrated in acetic acid and acetic anhydride, alcohols, and ketones[476,490-496]. The salts of polybasic organic acids (oxalic, tartaric, etc.) can be determined by titration in acetic acid[497]. Salts of organic bases[485,499] can also be titrated as bases in acetic acid[500,501], acetic anhydride[499], and acetic acid + acetic anhydride mixtures[485]. A method has been described for the determination of the combined acid in hydrazinium salts, based on the conversion of the hydrazine into the azine by reaction with acetone and titration of the resulting acid with NaOH solution[502].

2. Titration of Salt Mixtures

The use of non-aqueous differentiating solvents makes it possible to analyse salt mixtures[476,503,504]. Mixtures of salts, for example lithium and calcium acetates, potassium and zinc benzoates, sodium adipate and potassium hydrogen phthalate, etc., can be titrated as mixtures of bases with different strengths in ethyl methyl ketone[505] and in a dioxan + water (1 : 1) mixture[359]. Mixtures of salts can also be titrated as mixtures of acids with different strengths in pyridine[368] and methanol[1]. An interesting method has been developed for the analysis of two- and three-component mixtures of nitrates of the rare earth elements with the nitrates of other elements (Ni + La, Al + Eu, Cr + Tu, Fe + Zn + La, and Cr + Co + La) in a methanol + acetone medium[1]. A method has been developed for the analysis of multi-component mixtures of salts of organic acids, based on treatment of the mixture of salts to be analysed with perchloric or sulphuric acid in a medium of ethyl methyl ketone, followed by differentiated titration of the excess of perchloric or sulphuric acid and the acids liberated from the salts[312,506].

3. Titration of Mixtures of Salts with Acids or Bases

Mixtures of salts and acids can be analysed by direct potentiometric titration; for example, two-component mixtures of lithium chlorate and perchloric acid, or of sodium chlorate and benzoic acid, and also three-component mixtures of lithium and ammonium chlorates with perchloric acid can be titrated in pyridine[368], and a mixture of ammonium chloride and hydrochloric acid can be titrated in acetone[510-512].

Kreshkov, Yarovenko, and Milaev[1] developed a method for the analysis of mixtures of the rare earth elements, based on the conversion of the mixture to be analysed into the nitrates, bromides, or chlorides by the action of the corresponding acids followed by differentiated titration of the excess of acid and the mixtures of salts, which in an acetone + methanol medium behave as acids with different strengths (HNO_3 + Lu, HNO_3 + Lu + La, and HNO_3 + Dy + La).

Methods which have been developed for the analysis of salt mixtures, based on the preliminary treatment of the solution to be analysed with a stronger acid, can be used for the analysis of mixtures of salts with acids or bases[340-506-509]. This method can be used in a medium of ethyl methyl ketone for the titration of mixtures of sodium acetate and acetic acid, potassium benzoate and benzoic acid, and sodium acetate and acetic and salicylic acids, etc., and also mixtures of salts and bases, for example potassium benzoate and potassium hydroxide, sodium acetate, potassium salicylate, and sodium hydroxide, and other mixtures[505,508,509]. A method has been proposed for the analysis of mixtures of salts and acids, based on treatment of the mixture to be analysed with HCl solution followed by potentiometric titration of the resulting acids with an ethanolic solution of KOH[340].

A method has been proposed for the differentiated titration of mixtures of salts with hydrochloric, nitric, sulphuric, acetic, and other acids, based on the reaction of the mixture to be analysed with an excess of tetraethylammonium hydroxide solution; the excess of tetraethylammonium hydroxide and the hydroxide of the cation of the salt being analysed are then determined by potentiometric titration with a solution of perchloric acid in ethyl methyl ketone[513]. For the analysis of mixtures of salts of organic bases with

inorganic acids, we proposed a combined method[1], involving ion exchange and potentiometric titration of the mixture to be analysed in a medium of methanol.

4. Determination of Salts Using Ion Exchange

The use of ion exchange in non-aqueous solutions makes it possible to analyse various salt mixtures, and also mixtures of salts with acids or bases [514-521].

Yarovenko, Sayushkina, and Zelenina developed methods for the analysis of salt mixtures, based on the use of ion exchange in non-aqueous solutions. It is possible with H-cation exchange to determine mixtures of salts, whose acids can be determined by differentiated titration in non-aqueous solutions using the potentiometric method, for example, mixtures of the salts of strong inorganic acids such as sulphates + chlorides, sulphates + bromides, or sulphates + nitrates; mixtures of the salts of strong inorganic acids and weak organic acids such as nitrates (chlorides, bromides) + benzoates (salicylates, propionates, valerates, etc.); and mixtures of salts of organic acids such as salicylates + benzoates (propionates, etc.).

It is possible by OH-anion exchange to analyse mixtures of salts, whose bases can be estimated by differentiated titration in non-aqueous solutions. The use of anion exchange with Cl^- or NO_3^- forms can be used to determine mixtures of sulphates, chlorides, and nitrates.

VII. TITRATION OF MONOMERIC AND POLYMERIC COMPOUNDS IN NON-AQUEOUS SOLUTIONS

Titration in non-aqueous solutions has found extensive application for the analysis of monomeric and polymeric compounds.

1. Titration of Organoelemental Compounds

Non-aqueous solutions have found most extensive application in the analysis of organosilicon monomers and polymers. Kreshkov [522] developed the theoretical principles of the analysis of monomeric and polymeric organosilicon compounds in non-aqueous solutions and demonstrated the possibility of their practical application. Non-aqueous solutions can be used for the titration of alkylchlorosilanes [523,524], phosphorus-, boron-, sulphur-, and hydrogen-containing organosilicon compounds [525-535], alkylacetoxysilanes [536-538], silanols, and siloxanes [539]. A conductometric method has been described for the titration of trimethylchlorosilane, dimethyldichlorosilane, and methyltrichlorosilane in a medium of acetonitrile with organic bases containing tertiary nitrogen atoms (pyridine, quinoline, 8-quinolinol, dimethylaminoantipyrine, etc.)[523].

Drozdov and Tarasyants [531] developed a method for the potentiometric titration of alkylthiocyanatosilanes in the presence of alkylacetoxysilanes in a medium of acetonitrile. A method has been described for the analysis of boron-containing organosilicon compounds in the presence of organosilicon compounds containing chlorine and phosphorus [534].

The potentiometric and conductometric titration of alkylsilyl hydrogen phosphates in alcohols, ketones, and acetonitrile have been studied [527,529,530], and it has been established that triethylsilyl hydrogen alkylphosphonates can be determined quantitatively without preliminary separation in the presence of the corresponding triethylsilyl alkylphosphonate esters or alkylchlorosilanes. The behaviour of alkylsilanes, hexaalkyldisiloxanes, and sodium triethylsilanoxide in liquid hydrogen fluoride has been studied by an electrical conductivity method; the conductometric determination of individual alkylsilanols and hexaalkyldisiloxanes and their binary mixtures is possible [539].

Myshlyaeva and coworkers [540,541] developed a new method for the quantitative determination of silicon in organosilicon compounds, based on their decomposition with hydrofluoric acid followed by conductometric titration of the resulting hydrogen fluorosilicate in non-aqueous solvents with a solution of benzidine, tolidine, and other organic amines.

2. Titration of Monomeric Compounds

One method for the determination of unsaturated monomeric compounds is based on oxomercuration:

$$R_1R_2C=CR_3R_4 + Hg(OCOCH_3)_2 + CH_3OH \rightarrow$$
$$\rightarrow R_1R_2(OCH_3)C-CR_3R_4(HgOCOCH_3) + CH_3COOH.$$

Balyatinskaya and Tur'yan [542-544] used this reaction to determine the purity of vinyl derivatives of the pyridine series such as 2-methyl-5-vinylpyridine, styrene, methylstyrene, and 2,4-dimethylstyrene. The acetic acid liberated in the reaction in quantities equivalent to the concentration of the monomer being determined is titrated with a methanolic solution of KOH. The differentiated determination of cis- and trans-isomeric acids (fumaric and maleic, mesaconic and citraconic, and oleic and elaidic is possible [545]. The determination of the *cis*- and *trans*-isomeric forms of the acids involves determination of the total acidity and determination of the concentration of the *cis*-isomer by oxomercuration, followed by potentiometric titration of the unreacted mercury(II) acetate in non-aqueous medium. The rate of reaction of the *trans*-isomer with mercury(II) acetate is smaller by a factor of 20 than the rate of reaction of the *cis*-isomer.

A micro-method has been described for the determination of acetylenic hydrogen, based on the reaction of monosubstituted acetylenes with $AgClO_4$. The $HClO_4$ liberated is titrated with trihydroxymethylaminomethane solution [546].

Non-aqueous titration is finding application for the determination of the concentration of residual monomer in a polymer. Thus a method has been proposed for the determination of methylamine in melamine resins by titration of a specimen of the resin with an acetic acid solution of $HClO_4$ in an acetic acid + acetic anhydride (8 : 2) mixture using Crystal Violet as indicator. An analogous method can be used to determine the concentration of benzoguanamine in benzoguanamine resins. Guretskii and Toryanik [547] determined combined dibasic acids in polyester resins by potentiometric titration, in non-aqueous solutions, of the resin hydrolysis products.

3. Titration of Functional Groups in Organic Compounds

The concentration of carboxyl [371], alkoxy [548-551], hydroxyl [552-554], epoxy [291], dinitrophenyl [555] and other functional groups [556] in organic compounds can be determined in non-aqueous solvents.

Cundiff and Marcunas[549] developed a method for the determination of alkoxy groups, based on their reaction with HI to form the alkyl iodide, which in a medium of pyridine forms the alkylpyridinium halide; the differentiated titration of the latter and the excess of HI can be carried out with tetrabutylammonium hydroxide solution. For the determination of alkoxy groups in higher alcohols, a method has been proposed for the determination of the quantity of alkyl iodide formed, without its distillation[548].

A method has been described for the determination of hydroxyl groups[552] in organic substances in the presence of carbonyl compounds, ethers, amines, alkoxy compounds, and complex hydrocarbon mixtures by direct titration with aluminium and lithium amide in a medium of tetrahydrofuran. Hydroxyl groups can also be determined using 3,5-dinitrobenzoyl chloride[553], which reacts quantitatively with hydroxyl groups to form dinitrobenzoate, which can be titrated as a weak acid in a medium of pyridine.

A method has been proposed for the determination of compounds containing epoxy or ethyleneimine groups by titration in a medium of chloroform with a solution of perchloric acid in the presence of an excess of a quaternary ammonium bromide or iodide[291]. The concentration of acetoxy groups in various substituted acetoxysilanes can be determined by potentiometric titration in ethyl methyl ketone with a methanolic solution of sodium methoxide[536,537].

Titration in non-aqueous solutions is widely used for the determination of terminal functional groups in macromolecular compounds. This method is the most rapid and convenient for the determination of the molecular weights of linear condensation polymers whose molecular weight usually does not exceed 20 000.[557-559] Carboxyl[391,560,561], hydroxyl[562,563], and amino groups[254,391,564] can be determined. Carboxyl groups in polyamides can be determined by titration in a hot 2,6-xylenol + chloroform mixture[560] and in propargyl alcohol[391]. The chief disadvantage of these methods is the necessity to dissolve the polyamides at high temperatures, at which some of them decompose. For the determination of amino groups, the polyamides are dissolved in phenol + ethanol[564] and *m*-cresol + isopropyl alcohol (2 : 1)[391] mixtures. A method has been developed for the analysis of polymeric compounds of the benzimidazole series, based on the determination of the NH-group of the elementary unit of the polymer by titration in an ethyl methyl ketone + formic acid (4 : 1) medium[565]. Primary, secondary, and tertiary amino groups in polynuclear polyamines can be determined in non-aqueous solvents[269,456].

A method has been proposed for the determination of hydroxyl groups in macromolecular alcohols, the products of the addition of ethylene oxide to higher alcohols, and complex mixtures containing alcohols, alkanes, alkenes, esters, acids, and carbonyl compounds, based on acetylation with acetic anhydride in a mixed ethyl acetate + n-hexane solvent with the addition of perchloric acid as catalyst[562]. A similar method has been used to determine hydroxyl groups in polyoxyalkylene ethers[563]. Hydroxyl groups have also been determined in polynuclear phenolic compounds[566].

Guretskii and Rybal'chenko[567] proposed a rapid method for the determination of epoxy-groups in epoxy resins modified by organosilicon compounds. The method is based on the titration of the epoxy resins in a medium of acetic acid saturated with KBr solution, using an acetic acid solution of HBr as titrant. The addition of KBr to the solution makes it possible to increase considerably the rate of hydrobromination of the epoxy groups, Epoxy-groups have also been determined in non-aqueous solvents by other workers[568].

VIII. ANALYSIS OF INDUSTRIAL MATERIALS

Non-aqueous titration is being used successfully for the analysis of raw materials, intermediates, and finished products in the pharmaceutical and food industries, and also in the production of plastics, in the control of the various stages of industrial sulphonation, in the processing of coal, and in other industries. Methods for the titration of pharmaceutical products are particularly widely ployed[198,200,204,206,209,223,225,232,234,242,259,261,266,268,286,288,289,569-577]. Non-aqueous solvents can be used for the titration of not only individual pharmaceutical products with acidic or basic properties, but also their mixtures. Thus Izmailov and coworkers[571] analysed mixed products consisting of mixtures of weak acids (luminal, veronal, and aspirin) with weak bases (pyramidone, caffeine, and codeine). The bases were determined in a mixture of acetic acid and acetic anhydride (1 : 4) and the acids were determined in a mixture of dimethylformamide and benzene (1 : 3).

Titration in non-aqueous solutions is used for the determination of the concentration of antioxidants (*NN'*-disubstituted *p*-phenylenediamines) and polymerisation accelerators (diphenylguanidine) introduced into rubbers and rubber mixtures[233,446,578]. The bases to be determined are first extracted from the rubber mixtures using acetone. The concentration of aliphatic acids in rubbers is determined by a polarographic method[579].

Gribova and Khmel'nitskaya[264] developed a method for the analysis of an industrial mixture of mono-, di-, and tri-ethanolamines. Gribova[338] developed a method for the production control of 2,4-dichlorophenoxyacetic acid and also a method for the analysis of a sulphonation mixture containing sulphuric and sulphonic acids[344]. A method has been described for the analysis of explosive powders in non-aqueous solutions. The specimen is treated with dichloromethane and the concentrations of diphenylamine, 2-nitrodiphenylamine, 2,4-dinitrodiphenylamine, and N-nitrosodiphenylamine in the presence of one another are determined[220].

Emelin and coworkers[580] proposed a method for the determination of pyridine and nitrile nitrogen in the copolymer of acrylonitrile with methylvinylpyridine. Pyridine nitrogen in the form of the amine is determined in nitromethane by titration with perchloric acid solution, and the nitrile nitrogen is determined in dimethylformamide by titration with piperidine solution. The same authors also determined acetic anhydride in acetylating mixtures[454]. Rapid methods have been developed for the analytical control of the quality of crude phthalic anhydride obtained by the catalytic oxidation of naphthalene[581], and for the determination of n-butylamine in a caprolactam melt[270] and of tertiary amines in kerosene solutions[227].

A method has been described for the determination of sulphur in a gas by combustion in an atmosphere of oxygen followed by conductometric titration of the resulting sulphuric acid in aqueous ethanol[582]. Carbon dioxide obtained by the combustion of organic compounds is absorbed in dimethylformamide and titrated with a benzene–methanol solution of CH_3OK[583]. A method has been developed for the determination of traces of carbon in metals, alloys, and ceramics, based on the action of heat on the specimen in a current of oxygen, absorption of the resulting carbon dioxide in acetone, and subsequent titration[584].

The differentiated titration of ammonium nitrogen in ammonium salts and ammonium fertilisers can be carried out by back titration in acetone and other non-aqueous solvents[585-587].

Non-aqueous titrations were also used for the determination of pyridine bases in phenols[238] and of traces of acid in ethyl silicate[588] and surface-active substances[327,340].

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Contrast Intensification in the Electron Microscopy of Polymers

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CONTENTS

I. Introduction 298
II. Contrast in the electron microscope, and methods of increasing the contrast 298
III. Structural studies of polymers using contrast intensification methods. Effect of contrast materials 303

I. INTRODUCTION

The experience of recent years has shown that the properties of high-molecular-weight materials are determined essentially by their supermolecular structure. Therefore, information on the shape and size of regions of molecular aggregation of chains into bundle-like formations of different kinds is of interest. These structural features of polymeric materials can be investigated, mainly, by electron microscopy.

During the past decades, this method has produced a considerable volume of experimental data which has helped to correlate the properties of polymers with their structure. As a result, real improvements have been made in technological processes, but the problem is far from exhausted. The interlinking of amorphous and crystalline regions in polymers is still poorly understood. The mechanism of a number of transformations in polymeric materials (recrystallisation, polymorphic changes, etc.) has not yet been established. Further progress towards the clarification of these obscure areas of polymer science depends essentially on the development of high-resolution electron microscopy.

Currently available electron microscopes have a resolution of 4.5 Å, which allows crystal lattices with an interplanar spacing of ~ 2 Å to be photographed. However, the high resolving power of the electron microscope cannot always be exploited because of inadequate contrast in the image.

Image contrast in the electron microscope arises mainly from the scattering of electrons at the atoms of the object. Therefore, the contrast† of the electron-microscopic image is determined by properties of the object itself, such as density, thickness, and atomic number. If we fix the parameters of the electron microscope (aperture of the objective lens, accelerating potential) the contrast of the image increases in proportion to these properties of the object.

Organic materials do not meet the requirements for high contrast, because their molecules consist mainly of light atoms and their density usually lies in the range 1–2 g cm^{-3}.

Various methods, based on treating the object with substances containing heavy atoms of high scattering power, have been used to increase the contrast of electron-microscopic images of organic materials. These procedures have advanced most in the study of biological materials. Methods of contrast intensification for the electron microscopy of synthetic polymers are poorly developed, and have found only limited application.

An attempt has therefore been made, in the present article, briefly to review the contrast intensification procedures currently used for synthetic polymers and for biological materials. This is followed by a discussion of work on the morphological structure of polymers involving contrast enhancement by treatment with suitable materials.

Since contrast materials can modify the structure as well as reveal it, we shall consider the influence of contrast materials on the structure of an object being examined in the electron microscope. The review will begin with a short discussion of the dependence of image contrast on the parameters of the electron microscope and on the properties of the specimen.

II. CONTRAST IN THE ELECTRON MICROSCOPE AND METHODS OF INCREASING THE CONTRAST

Depending on the mechanism of image formation, we can distinguish between amplitude contrast and phase contrast in the electron microscope[1–3]. When an electron microscope is operated in the normal way without special attachments, phase contrast is produced by phase shifts arising from: (1) defocussing, and (2) spherical aberration. In addition, diffraction contrast due to the ordered arrangement of the atoms[4–10] can arise, in the study of crystalline materials, as a result of phase shifts.

Although phase shifts can increase the contrast to some extent, they add to the difficulty of a quantitative assessment of the image contrast because of their ambiguity.

At the present time, amplitude contrast plays the most important part in electron microscopy: it provides the basic information on the morphological structure of the object. Electron absorption makes an insignificant contribution and is ignored in practice[11–15].

Electrons which are scattered through angles greater than the aperture are absorbed by the diaphragm of the objective and do not take part in the formation of the image. Only those electrons which pass through the specimen unscattered, or scattered through small angles, contribute to image formation. Hence, the intensity of the electron beam is decreased after passage through the specimen. The intensity at the image of the specimen‡ can be expressed in the form

$$I = I_0 e^{-\frac{N_A}{A}\sigma_a \gamma x}, \qquad (1)$$

where N_A is Avogadro's number, A the atomic weight, γ the specific gravity of the object, x its thickness, I_0 the

† The term refers to the amplitude contrast of the image.

‡ The specimen is assumed to be amorphous.

intensity of the incident beam, and σ_α the effective cross-section of the atom. The contrast K of the electron microscope image is defined as the relative intensity of the electron beams I_1 and I_2 passing through neighbouring areas:

$$K = \frac{I_1 - I_2}{I_1} = 1 - \frac{I_2}{I_1}. \quad (2)$$

By combining Eqns. (1) and (2) we obtain an expression for the contrast K in terms of parameters of the object, in the form

$$K \simeq N_A \left(\frac{\sigma_{\alpha_2}}{A_2} \gamma_2 x_2 - \frac{\sigma_{\alpha_1}}{A_1} \gamma_1 x_1 \right). \quad (3)$$

This equation shows that contrast in the image arises as a result of differences in: (1) the scattering power of the atoms of the object, (2) the thickness, and (3) the density of the object.

The scattering power of an atom is characterised by the effective scattering cross-section σ of the atom. The effective cross-section of interest in electron microscopy is σ_α, which defines the probability of electrons being scattered at that atom by angles greater than the angular aperture α_0.[13,16-19] This is because the image is formed only by those electrons whose scatter angles lie within the angular aperture α_0 of the objective lens.

σ_α is a function of the atomic number Z, of the angular aperture α, and of the accelerating potential U. Since σ_α appears in the equation which defines the contrast, the latter depends on Z, α, and U as well as on γx; in other words, the contrast depends both on the observation conditions in the electron microscope and on the atomic number of the specimen.

It should be noted that the cross-section which appears in the contrast equation is the total cross-section $\sigma_\alpha = \sigma_{e\alpha} + \sigma_{u\alpha}$ (the sum of the effective cross-sections for elastic scattering, $\sigma_{e\alpha}$, and for inelastic scattering, $\sigma_{u\alpha}$, of electrons[20-22]).

1. Variation of Contrast with Accelerating Potential

A decrease of image contrast with increase of accelerating potential is a general feature of electron microscopy.

It has been stated[23,24] that the contrast is inversely proportional to the accelerating potential, or directly proportional to the square of the wavelength λ, since

$$\lambda = \frac{12.225}{\sqrt{U}} \text{ Å}.$$

However, a linear dependence of contrast on accelerating potential is only a special case, and can be realised only under certain observation conditions. In the more general example, the contrast is a power function of U, and therefore of λ^2.[24] The effective scattering cross-section which characterises the contrast is expressed in the form

$$\sigma_\alpha = A(\lambda^2)^l,$$

where A is a coefficient, l is an exponent depending on the particular apparatus, and λ is the wavelength.

Hence, it is desirable to lower the accelerating potential in order to improve the contrast. This problem has been discussed by many workers. Thus, Valentine[25] states that in microscopes with an accelerating potential of 5–6 kV the contrast is higher by a factor of 10 (as compared with 50–60 kV microscopes).

Some low-voltage electron microscopes have already been developed. Nixon[26] reports a considerable improvement in the image contrast by using an accelerating potential of 6 kV. However, the large gain in contrast offered by low-voltage electron microscopes cannot be fully exploited when the image is recorded on conventional photographic materials, because electrons of 6 kV energy cannot penetrate into the bulk of the emulsion, and this causes a loss of contrast in the photographic plate.

The use of electro-photography in low-voltage electron microscopes may enable the possibilities of the technique to be more fully realised. The first experiments in this direction, using electron beams of intermediate energies for electro-photography, have shown that the sensitivity of the method cannot compete with that of the more conventional methods of recording electron microscope images[27,28]. Nevertheless, low-voltage electron microscopes already offer improvements in contrast; these can be achieved by the use of various attachments to the electron microscope. In particular, the brightness intensifier not only allows the range of intensities of illumination of the object to be extended, but it also influences the contrast of the image. Existing methods of contrast intensification in electrophotography may also find application in electron microscopy, by using special photo-recording materials.

When organic materials are examined in a low-voltage electron microscope, allowance must be made for the increased thermal and radiation-chemical effect of the electron beam when the accelerating potential is decreased[29-34]. Thus, it is thought[23,35] that the optimum accelerating potentials for the electron microscopy of organic materials lie in the range 30–40 or 30–60 kV.

2. Variation of Contrast with the Angular Aperture of the Objective Lens

The general rule is that the contrast increases when the angular aperture of the objective lens is decreased. The variation of contrast with α_0 is strongly dependent on the atomic number Z of the material under examination[36-38]. In particular, it has been pointed out that the effective scattering cross-section σ_α (and therefore also the contrast) falls of rapidly with the angular aperture α_0 when Z is small. For large Z the decrease of σ_α with α_0 is more gradual.

For thin layers, and in the range of angular apertures $3 \times 10^{-4} < \alpha_0 < 1.7 \times 10^{-2}$, the relative change in contrast can be expressed in the form

$$\frac{K(\alpha)}{K(0)} = \frac{n_e}{n_e + n_u} \left[\frac{1}{1 + \left(\frac{\alpha_0^2}{\chi_0} \right)} + \frac{n_u}{n_e} \left(0.89 - 0.5 \ln \frac{\alpha_0}{3 \cdot 10^{-4}} \right) \right],$$

where $K(0)$ is the optimum contrast obtainable with $\alpha_0 > 0$; n_e and n_u are the numbers of elastic and inelastic collisions between electrons and the atoms of the object. Also,

$$\chi_0 = 0.84 Z^{1/3} \frac{\sqrt{1-\beta^2}}{\beta} \cdot 10^{-2}.$$

Fig. 1 shows the variation of the relative contrast $K(\alpha)/K(0)$ of the image of thin carbon films ($Z = 6$) with the aperture α_0 of the objective for two values of the accelerating potential, $U = 40$ kV and $U = 100$ kV.[17]

The aperture of the objective, α_0, is determined by the diameter of the aperture diaphragm of the objective lens, by the focal length of the objective, and also by the spherical aberration constant. Valentine has found that the contrast is doubled by changing the diaphragm diameter from

50 to 10 μm. However, extremely small diaphragm orifices rapidly become contaminated, giving rise to astigmatism. For this reason, Valentine recommends the use of diaphragm orifices 25 μm in diameter[23].

In Leisegang's book[17] changes in the accelerating potential and in the aperture of the objective are compared as methods for enhancing the contrast. The author considers it more satisfactory to increase the contrast by lowering the accelerating potential than the angular aperture. For a given object, he shows that the same contrast can be obtained at: (1) $U = 100$ kV, $\alpha_0 = 3 \times 10^{-4}$, and (2) $U = 40$ kV, $\alpha_0 = 10^{-2}$. However, under the former conditions the loss of resolution of the electron microscope is greater than in the latter.

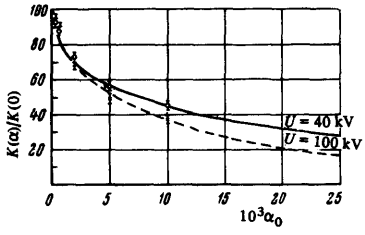

Figure 1. Relative contrast $K(\alpha)/K(0)$ of the image of thin carbon films against the aperture of the objective α_0 for two values of the accelerating potential[17].

Thus, the contrast of the image depends to a great extent on the conditions under which the object is observed. In order to obtain the maximum amount of information on the structure of the object with the help of an electron microscope, the optimum observation conditions should be provided. Pilyankevich has constructed a nomogram[42] which helps to choose the best experimental conditions.

3. Variation of Contrast with Atomic Number

As a general rule, the contrast increases with the atomic number Z[39-42].

The variation of the effective scattering cross-section σ_α with Z can be expressed in the form

$$\sigma_\alpha = AZ^k, \qquad (5)$$

where A and k are constants depending on α_0 and U. On increasing the angular aperture α, the variation of σ with Z tends to a quadratic form[3]. The linear variation of σ with Z is a special case, which applies only for particular values of the microscope parameters[17].

On this general rule is superimposed a periodic variation of the effective scattering cross-section with atomic number Z, which becomes less pronounced as the angular aperture of the objective increases[16,17]. Fig. 2 shows the periodic variation of σ with Z according to Pilyankevich[13]. Hence, not only the atomic number Z but also the position of the element in the periodic curve of σ_α against Z must be considered when calculating the contrast. It follows from Fig. 2 that the greatest contrast can be expected from substances such as iridium, osmium, rhenium, platinum, tungsten, gold, tantalum, chromium, uranium, and palladium, that is, elements for which the effective scattering cross-section lies on the peaks of the curve.

The amount of material needed to produce a standard contrast depends on the atomic number. Thus, the same contrast is obtained with a 50–70 Å layer of chromium, an 8–10 Å layer of gold, or a 3–7 Å layer of platinum or palladium[18].

4. Variation of Contrast with Density and Thickness of the Object

If the object consists of atoms of identical scattering power, image contrast can arise only as a result of differences in mass thickness (the product of thickness and density) of two adjacent areas[43-48]:

$$K = \frac{N_a \sigma_a}{A}(\gamma_2 x_2 - \gamma_1 x_1).$$

The molecules of most synthetic polymers and biological materials consist mainly of light atoms. Since N, C, and O atoms have practically the same scattering power, the

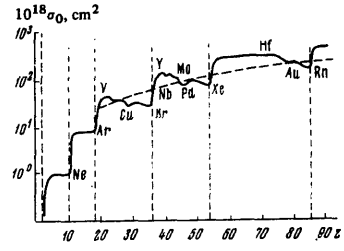

Figure 2. Variation of the effective scattering cross-section σ_0 with the atomic number Z of the elements[13].

image contrast of organic objects is due either to thickness variations or to density variations in the object being examined.

What is the thickness or density difference in an organic object needed to ensure the minimal contrast of the image which can be reliably recorded on photographic materials? (The minimal contrast for photographic materials is $K_{min} = 0.1$.) Valentine and Horne consider that if the product of thickness (in Å) and density (in g cm^{-3}) is greater than 400 the object will be distinctly visible, although a product greater than 100 is sufficient for the object to be detected on the photograph[49]. In the same paper it is shown that a photographic plate will not detect a difference in contrast for two materials of density 1.05 and 1.5 g cm^{-3} respectively: in other words, a density difference of 30% is insufficient to ensure appreciable image contrast.

Since density fluctuations in synthetic polymers and biological objects are usually much lower than this figure, the image contrast is affected almost exclusively by the thickness of the object.

The minimal thickness of an organic object which can be reliably recorded photographically has been discussed by many workers[46,47,50], who find that a thickness of at least 50 Å is necessary for satisfactory recording on a photographic plate. Elsewhere, figures of 100 Å are quoted. These values apply to electron microscopes of intermediate electron energies.

Pilyankevich and Stoyanova[24] investigated the minimal thickness Δd compatible with appreciable contrast as a

function of the accelerating potential of the electron microscope. They found that for $U = 50$ kV the minimal thickness is $\Delta d = 50$ Å (assuming $\rho = 1$ g cm^{-3}), whereas for $U = 200$ kV Δd increases to 500 Å. This means that the higher the accelerating potential, the greater must be the thickness of organic objects to be examined in the electron microscope. However, these results apply to the normal mode of operation of the electron microscope with image formation under bright field conditions. For dark-field images, the variation of the contrast with γ_x follows a different law, discussed in the work of Pilyankevich and Stoyanova. It is found that the dark-field offers a higher contrast than the bright-field method when the specimens are either very thin or very thick [51-54].

Thus, the potential use of electron microscopy in the study of organic materials meets with serious limitations associated with the contrast problem. Minor density changes in synthetic polymers and biological materials are not detected by the electron microscope. Hence, the contrast of organic objects reflects, essentially, only thickness variations in the material under study:

$$K = \frac{N_A \sigma_a}{A\gamma}(x_2 - x_1).$$

Consequently, materials which can be prepared as fine particles (more than 50 Å thick) are the most convenient for the electron microscopy of organic objects without contrast intensification.

In studies of ultra-thin sections having uniform thickness, the image contrast is practically the same in different parts of synthetic polymer or biological sections, giving no information on the morphological structure of these materials unless they are specially treated. Only rarely have differences in contrast of the sections been detected as a result of slight differences in thickness arising from specific features of the method of preparation (for example, in washing the section free from the mounting medium, etc.).

Similar difficulties, due to inadequate contrast, arise also with methods of preparation of organic objects other than the ultra-thin section method.

Various methods of treating the object with substances containing heavy atoms of high scattering power have been used to increase the image contrast of organic materials. The oldest and best developed method of contrast intensification is the shadowing method, which consists in depositing on the object a thin layer of metal, evaporated in a vacuum at a glancing angle to the object. The shadowing method was one of the first contrast intensification procedures, and is still widely used. It was first suggested by Williams and Wickoff [55] in 1944, and is now often applied in electron microscopic practice. However, this method allows one only to reveal the shape of the object and to reproduce the structure of its surface. Furthermore, in high-resolution work the structure of the evaporated layer itself becomes intrusive. The grain size of the evaporated material varies with the nature of the chosen metal and the method of shadowing used. A vast amount of literature has accumulated, both on the shadowing method itself and on its application to organic materials including biological specimens and synthetic polymers. The method is discussed in detail in monographs on electron microscopy [56,57].

Work on the method has been aimed mainly at finding a material and a shadowing technique to give a smaller grain size whilst retaining a high contrast. A relationship between grain size and the identity of the evaporated material has been demonstrated [58,59] in a study of a number of materials for shadowing electron microscopic objects. It is stated that the smallest grain size (down to 15 Å) can be obtained with platinum. The grain size can be brought down also by using special capillaries through which the metal vapour is directed at the object [60]. Noteworthy among these papers is that of Galyanov, who proposed a shadowing technique in which the metal is sputtered in a gas discharge, this allows the grain size to be decreased substantially [61]. Shadowing is used also when the object is examined by the replica method, as in the case of thick samples opaque to electrons. The commonest replica materials are quartz and carbon, both of which have a low scattering power. Hence, in order to increase the contrast, the replicas are shadowed with metals. In this method the quality of the replicas is determined essentially by their resolution. Bradley reports [62] that high-resolution replicas can be obtained by simultaneous evaporation of carbon and platinum. Marikhin obtained good results by evaporating quartz and platinum together [63]. Replica methods are described in detail in special articles and also in books on electron microscopy.

In the present article, however, we shall not dwell on this work, because we are concerned only with problems of contrast in direct examination, that is, in studies of the object itself rather than of its imprint.

Furthermore, we shall be concerned primarily with contrast intensification methods in which the object is impregnated with substances containing heavy atoms of high scattering power. These methods have been developed mainly in studies of biological objects, and have yielded more meaningful information on the morphological structure of these materials than has the shadowing method. In the field of synthetic polymers, the impregnation methods of contrast intensification are less well developed and have not been widely used. We shall therefore devote the major part of this article to those methods. Contrast intensification procedures which have been applied only to biological materials will be briefly mentioned.

Methods of contrast intensification involving impregnation of the object with materials containing heavy atoms were originally termed electronic staining, or simply "staining" methods, because of the obvious analogy with optical microscopy.

The term "staining" is now used mainly in the foreign literature, whereas "contrast intensification" is used in the Soviet literature.

The following methods of contrast intensification (or staining) in the study of organic materials by electron microscopy are known: (1) positive contrast intensification; (2) negative contrast intensification; (3) immunochemical contrast intensification; (4) the autoradiographic method; (5) the development of ordered regions; (6) the silver ion reduction method; and (7) decoration.

Positive contrast intensification or positive staining was one of the first methods for enhancing the contrast of organic objects [64,65]. Originally it was simply called "staining", but when a new method of contrast intensification (termed "negative contrast intensification") was developed, it became known as positive contrast intensification or positive staining. The method consists in impregnating the object with salts of heavy metals, and has been used with biological objects. In multicomponent structures, contrast is generated by the different amounts of metal which penetrate selectively into the structural elements of the object. Thus, osmium gives good contrast with lipoid structures, uranyl acetate with nuclei acids.

Negative contrast intensification (*negative staining* [69]) was first described towards the end

of the 1950's, and quickly became popular[66-70]. The principle of the method is that the particles being examined are surrounded with (or "*embedded*"[62] in) a strongly electron-scattering material, producing a contrast opposite to that obtained by positive staining. The negative staining method has been applied both to synthetic polymers and to biological polymers.

Immunochemical contrast intensification (*immunochemical staining*) is applied exclusively to biological objects[71]. The method depends on the binding of antibodies with antigens. Antigens (for example, virus antigens) become visible in the electron microscope if antibodies specific to the virus particles are previously chemically combined with proteins containing heavy atoms. Ferritin, which contains an iron atom, is frequently used as the protein. When the antibodies become bound to the antigens, the latter develop a higher contrast, which allows their location in the cell to be identified. The sensitivity of this method is extremely high.

The autoradiography method consists in treating the object with radioactive materials, which segregate at specific points[72,73]. A photosensitive layer similar to a photographic emulsion and containing silver atoms is then deposited on an ultra-thin section of the object. After exposure and photographic development of the object, silver particles are deposited on the parts of the cell where radioactive elements are present. The contrast of some of the cell structures is increased, so that they can be seen in the electron microscope. This method, also, is confined to biological objects.

The development of ordered regions is applied to oriented synthetic fibres. The object is impregnated with salts of heavy metals, which concentrate in the disordered regions of the fibre[74,75]. The object is pre-treated with reagents able to loosen the amorphous, disordered regions, thus assisting the penetration of the contrast-producing agent into those regions (but not into the ordered regions).

Contrast intensification by the reduction of silver ions has only recently been proposed. So far, it has been used and investigated only with graft polymers, guanine, poly(acrylic acid)[76], and DNA. The principle of this method is as follows. When the object has been treated with salts of heavy metals (for example, silver), silver crystals are deposited at the active groups of the polymer chain. The process is reminiscent of the formation of silver crystals during physical development. Since the silver nuclei have ~ 50 Å dimensions, we are able to see in the electron microscope the location of the specific groups of the polymer on which a hydrogen ion has been replaced by a silver ion, even though the silver atom itself does not meet the minimal requirements for contrast and is therefore invisible.

The decoration method has been adequately developed for inorganic crystals, in which it allows surface heterogeneities to be made evident[99,100]. The method is relatively simple, and consists in the high-vacuum evaporation under stated conditions, onto the surface of the object, of a metal (such as gold) whose particles can "label" the surface heterogeneities. This method has found practically no application in the study of organic materials. Only very recently has a preliminary report appeared of work by Bassett and coworkers on displaying the defects of the folded surface structure of polyethylene single crystals grown from solution.

Of all these methods, the negative contrast intensification method has attracted most attention in recent years for the electron microscopy of biological objects and synthetic polymers. A great deal of work has been published, particularly in the field of biology, using this method. Many workers have studied the method and have attempted to develop it further. Valentine and Horne[49], and Bradley[77] have reported some interesting studies of the negative contrast intensification method, of the materials used in it, and also of the resolution which can be expected from the method.

Somewhat conflicting views on the resolution of the negative contrast method have been published. Brenner and Horne[69] initially estimated the resolution as 15 Å. However, from recent microphotographic results, Bradley[77] obtains a resolution of 30 Å, reaching 15 Å only in special cases. Valentine and Horne quote figures of 20–30 Å[49]. Kay's book[57] states that details below 20 Å cannot be reliably investigated by negative contrast intensification.

Many workers have discussed the nature of the negative contrast intensification process, but a clear understanding of the interaction between the contrasting agent and the object is still lacking. Brenner, Valentine, Horne, Hall, and Bradley have all made interesting contributions in this area[43,49,50,69]. A paper by Müller and Meyerhoff[78] describes the "anomalous" contrast observed in negative contrast intensification: crystallites of MgO, deposited on a layer of tungstophosphoric acid, produce brighter areas in the image than the layer of contrast material. They ascribe this unusual effect to charges in the object itself. Later, Lippert studied the phenomenon in more detail by measuring the electrons scattered from the object and from the tungstophosphoric acid (TPA) during negative contrast intensification[79]. His experiments disprove Müller and Meyerhoff's hypothesis: Lippert considers that the "anomalous" contrast arises from the relative positions of the object and the TPA rather than from charges in the object. An MgO crystallite deposited on a layer of TPA is drawn into it, and scatters fewer electrons than the surrounding area of TPA. Thus, the "anomalous" contrast disappears, since the density distribution of scattered electrons in the image now varies in the same sense as the mass–thickness product of the object.

Phenomena leading to a loss of contrast also have to be considered in the electron microscopy of organic materials. In particular, a serious obstacle to the study of low-contrast objects is contamination by hydrocarbon vapours deposited on the object from the microscope column, which can lead to the formation of a thin film under the influence of the electron beam. A great deal of work has been done on this problem[80-84], but a discussion of this work would be out of place in the present review. The most recent designs of microscopes already include special attachments for minimising the rate of contamination of the specimen, and this undesirable phenomenon can now be readily overcome.

Thus, the contrast of the image of an organic object can be enhanced either by using the facilities offered by the electron microscope itself or by treating the object with materials of high scattering power. Since the optimum operating conditions in electron microscopic practice are usually chosen for fixed values of the apparatus parameters, most of the published work in this area deals with the problem of contrast intensification in the study of synthetic and biological polymers.

Published studies of biological objects and synthetic polymers by contrast intensification methods show that most of the effort is concentrated on revealing the fine structure of the specimens. The influence of the contrast agent on the specimen is attracting rather less attention, particularly in studies of biological polymers. However, the interaction between the contrast agent and the object is discussed in a number of papers. Therefore, we shall consider in detail not only the structural data obtained by electron microscopic studies of polymers but also the effect of the contrast-producing material on the objects being examined.

III. STRUCTURAL STUDIES OF POLYMERS USING CONTRAST INTENSIFICATION METHODS. EFFECT OF CONTRAST MATERIALS

Synthetic Polymers

The earliest electron microscopic studies of synthetic fibres using contrast intensification methods are due to Hess and his coworkers [74,75,85-89], who tried to detect large network spacings by electron microscopy. Large spacings had previously been observed in most synthetic polymer fibres by low-angle X-ray diffraction. Since the observed large spacings, of the order of 70–200 Å, did not match the length of any of the chemical groupings present in the polymers, it was suggested that superlattices appear in these materials as a result of the periodic alternation of ordered and disordered regions in the polymer. The sum of the lengths of these regions was identified with the observed large spacing. Large spacings were reported in fibres of polyethylene, poly(vinyl alcohol), and in polyamide fibres [89,90]. These materials were therefore investigated in the electron microscope with the aim of displaying the large spacing directly on the photographic plate.

It is well known that the density difference between amorphous and crystalline regions in polymers does not usually exceed 10%, which is not enough to provide the minimal contrast required in the electron microscopic image when working with electrons of intermediate energies, that is, under the normal experimental conditions. Therefore, the polymers were treated with materials containing heavy atoms of high scattering power, before being examined in the electron microscope, in order to enhance the contrast.

Essentially, these workers sought to increase the contrast by virtue of differences in the ability of amorphous and of crystalline regions of the polymers to sorb materials containing heavy atoms, thus producing enhanced contrast between the different regions of the specimen.

In an electron microscopic investigation of poly(vinyl alcohol) fibres, the specimens were treated with iodine after being steeped in formalin [74]. Large spacings of the order of 150 Å were revealed, as well as superspacings of the order of 700 Å. Examination of these fibres by X-ray diffraction confirmed a periodicity of 160 Å, but not the 700 Å superspacing.

Hess and coworkers used tungstophosphoric acid as the contrast enhancing material in their studies of polycaprolactam fibres [87]. The specimens were pretreated with a solution of HCl, which loosened the fibres and assisted the penetration of the contrast intensifier. These workers made a comparative study of the sorption of TPA in synthetic polymers and in collagen fibres. In the latter, the fine structure was developed by the chemical combination of a functional group of the protein molecule with TPA, which remained firmly held during the subsequent washing. In polycaprolactam fibres the TPA was sorbed only under special conditions (after swelling in a 9–10% solution of HCl).

The authors also studied the effect of HCl on the large spacing of polycaprolactam, and showed that the treatment produces a 30% shrinkage of the fibre length. Swelled fibres give more intense X-ray reflections, and their large spacing increases from 70 to 100 Å. After being pretreated with HCl solution, the fibres were dried and washed and treated with a 2% solution of TPA for 48 h. Under these conditions, sorption of TPA and penetration of contrast intensifier into the fibre takes place. The amount of TPA taken up was a function of the concentration of the HCl, that is, of the degree of swelling of the fibre.

High-angle X-ray diffraction studies of the treated fibres showed that the TPA is absorbed only by the disordered regions of the fibre, the crystallites remaining unaffected. The reflections also became stronger, indicating fewer defects in the crystal lattice and a higher degree of order. From the low-angle diffraction observations on treated fibres it was clear that the intensity of the meridian reflections increases with the concentration of the HCl. As the amount of TPA absorbed in the fibre increases, new reflections corresponding to 40–45 Å and 20–25 Å appear (the spacing is 70–90 Å at 9% absorption of TPA, 40–50 Å at 18% absorption).

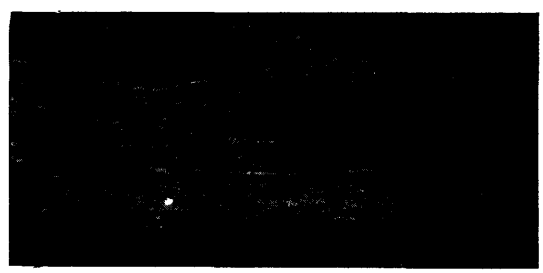

Figure 3. Polycaprolactam fibre stained with TPA [87].

Electron microscopic pictures of the dispersed fibres after treatment with HCl and TPA show that the fibre consists of thin fibrils 50–100 Å wide (Fig. 3). Along the fibrils, spacings of 70–90 Å can be distinguished as an alternation of light and dark bands. The authors point out that the periodicity along the fibre appeared only after treatment with HCl. The large spacing obtained from the X-ray diffraction work coincides with the value given by the electron micrographs.

Comparing the results of the electron microscopy of synthetic and natural fibres, Hess suggested that polycaprolactam is a better model of a protein fibre than poly(vinyl alcohol) or cellulose. This is because the material contains ϵ-aminohexanoic acid, which can react with the contrast intensifier TPA) to produce an electron microscopic image similar to that of collagens.

In 1958, a new method of contrast intensification was introduced into electron microscopy. The method, termed negative contrast intensification, has been widely applied in studies of biological objects. It has also been used by the present writers in studies of synthetic polymers [91-93]. Unlike Hess, who used TPA, we treated our specimens with

the potassium salt of TPA using the procedure suggested by Brenner and Horne[69] for biological objects. No pretreatment of any kind was given to the synthetic fibres. Contrast was achieved with both dispersed and ultra-thin sections of polycaprolactam, Lavsan [Dacron (Ed. of Translation)], and polyethylene fibres.

We had previously investigated the effect of TPA and its potassium salt on the structure of a number of synthetic fibres. The effect of the contrast agent was established by high-angle and low-angle X-ray diffraction, and also from electron microscopic and gravimetric data. From the normal high-angle diffraction patterns, the structure and the orientation of the crystallites in the fibres appeared to be unaffected by treatment with TPA or its potassium salt. Some changes were observed under low-angle diffraction. The intensity distribution curves obtained in an ionisation apparatus for treated and for untreated polycaprolactam fibres were used to calculate the large spacing and the size of the crystallites and of the amorphous regions[94]. The large spacing increased from 92 to 99 Å following treatment with 2 and 20% TPA respectively, the increase being due mainly to an increase in the size of the crystallites. The high-angle diffraction pattern of the fibre was unaffected by treatment in 20% TPA solution. An increase in weight not exceeding 5%, due to absorption of TPA, was observed by weighing the fibres after lengthy treatment in 20% TPA.

Electron micrographs of fibres which had not been washed after being treated with TPA showed extensive absorption of the staining agent, leading to a general increase in the level of intensity but making the structural elements indistinguishable.

Figure 4. Dispersed polyethylene fibre, stained with the potassium salt of TPA[94].

The elements of the fine structure of the fibres were revealed only by treating the dispersed fibres with the potassium salt of TPA. The photomicrographs of a polyethylene fibre (Fig. 4) treated in this way show a system of parallel fibrils, made visible no doubt by the penetration of the TPA salt into the regions between fibrils. The width of the fibrils was constant for different fibres (70–80 Å). A similar system of fibrils was observed in a section of a Lavsan [Dacron] fibre which had been treated with the potassium salt of TPA. It should be noted that the fibrillar picture of the longitudinal section gives an idea of the structure of the compact material of the whole fibre before disintegration by ultrasonic waves. From these results, we were able to conclude that the potassium salt of TPA has no effect on the value of the large spacing, it does not affect the crystallites, and it penetrates only into the interfibrillary spaces and the amorphous regions, in minute amounts. Nevertheless, these amounts of TPA are sufficient to reveal the fine structure of the polymers on the electron micrographs. It is pointed out that TPA (unlike its potassium salt) affects the large spacing, albeit by a small amount. Furthermore, TPA penetrates the fibre extensively, raising the level of the contrast but obscuring the fine structure.

For these reasons, we used the potassium salt of TPA as a contrast intensifier to reveal the large spacing in synthetic polymers. However, we met some difficulties: the minute amounts of contrast material sorbed by the amorphous regions were not always sufficient to provide the minimal contrast needed in the electron microscopic image. Hence, our observations of large spacings did not extend to all parts of the specimen, but were confined to those regions where the concentration of the potassium salt of TPA happened to be high enough, but not so high as to obscure the structure. A large spacing was observed in the micrographs of the following dispersed synthetic fibres: polycaprolactam, Lavsan [Dacron], polyethylene, and pyrolysed polyethylene. The electron microscopic results agreed well with those obtained by X-ray diffraction. TPA was found to be an excellent contrast agent also for single crystals of polyesters. One of our papers[93] describes contrast intensification in polyester single crystals and spherulites. The latter clearly show a fibrillar structure with TPA contrast (Figs. 5*a* and 5*b*).

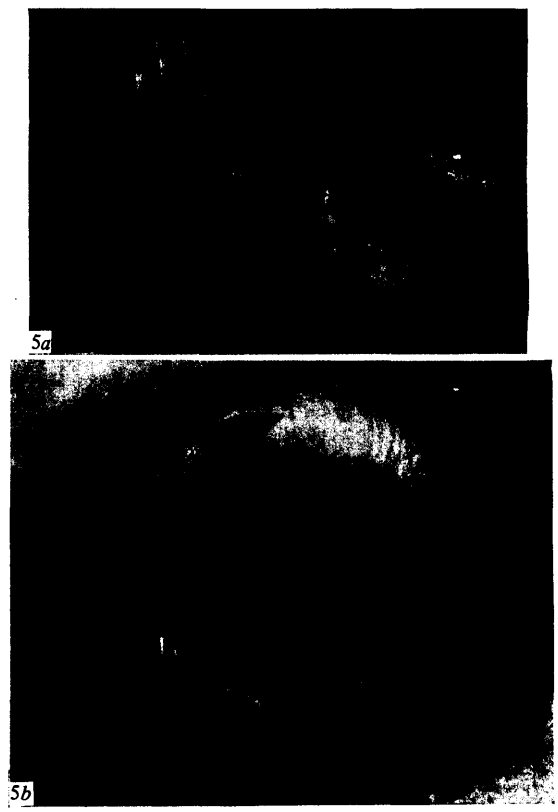

Figure 5. Negative contrast intensification of a polyester preparation[93]:
a) single crystals; *b*) spherulite.

TPA was also used by Spit[95] as a contrast material for thin films of nylon, consisting of spherulitic structures with dark and light bands (revealed by the contrast treatment) of width equal to the known large spacing of the polymer under study.

Osmic acid (OsO_4) is often used as a contrast material in the electron microscopy of biological objects, because it has fixing as well as contrast properties. Marikhin and coworkers[96] investigated the contrast properties of OsO_4 on polymers by the low-angle X-ray diffraction method. They found that the intensity of low-angle reflections does not vary monotonically with the concentration of sorbates (iodine and OsO_4). The high-angle X-ray diffraction pictures show that these sorbates are concentrated in the amorphous regions of the polymers.

When multicomponent polymer systems are examined in the electron microscope, there are difficulties in revealing each individual component in the micrograph, because the polymers consist of light atoms having practically identical scattering powers. The inadequacy of the contrast raises special difficulties in work with ultra-thin sections of multicomponent structures, such as graft polymers. To distinguish between the different types of polymer in a graft fibre, a method of contrast intensification has been proposed for which we suggested the term "contrast intensification by reduction of silver ions"[76,97,98].

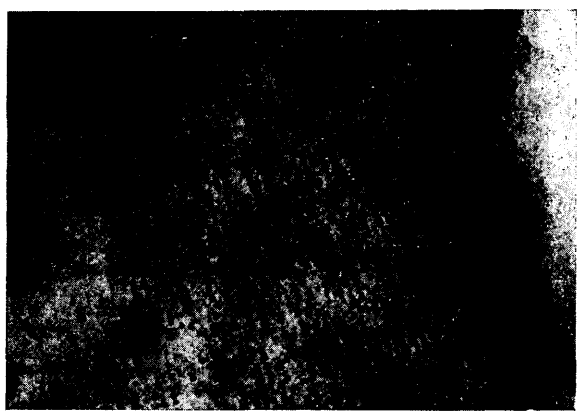

Figure 6. Cross-section of a polycaprolactam fibre treated with $AgNO_3$.[98]

The possibility of producing contrast in these polymers was demonstrated by the present writers by working with polycaprolactam fibres modified with poly(acrylic acid). The fibres were treated with salts of heavy metals: they were boiled for 3 h in saturated solutions of $AgNO_3$ and $HgNO_3$, causing partial replacement of carboxylate ions by heavy metal ions. By virtue of the powerful scattering effect on electrons of the Ag and Hg atoms, the location of the grafted material could be identified. An electron micrograph of the cross-section of a polycaprolactam fibre is reproduced in Fig. 6, where contrasting particles of 50–70 Å dimensions are clearly visible. The number of contrasting particles can be correlated with the percentage of grafted material, and decreases as the polymer being grafted penetrates into the bulk of the host polymer. In a polypropylene fibre with 5% of grafted material the number of particles is quite small. Dark-field observation of these particles showed them to be crystalline[98]. We have shown that the deposition of crystalline silver at the active groups of the polymer chain is not unlike the process of physical development in photography. Obviously, the first nuclei of the silver crystallites are formed at the poly(acrylic acid) sites, and this enables the disposition of the grafted polymer molecules to be seen in the electron micrograph. It was concluded from this work that the mechanism of this method of contrast intensification is similar to the mechanism of oxidation–reduction reactions.

Thus, contrast observation in ultra-thin sections can reveal the morphological structure of the object, but this cannot be done without special treatment of the object. In a few special instances, however, the fibril structure of fibre sections can be observed without artificial contrast thanks to differences in thickness between the different parts of the object, which can be observed after special preparative techniques[101].

Cellulose

The early electron microscopic studies of cellulose were made in the 1940's, before the preparation and staining techniques had been fully developed. The object was prepared by coarse mechanical comminution[102,103], and good preparations, transparent to electrons, were difficult to obtain. The specimens were in no way stained, and the image contrast was determined by differences in thickness only. Because of the low level of the preparative techniques, only a negligible amount of information on the structure of cellulose was gained from the electron microscopic results. The very first studies of cellulose by electron microscopy, reported by Ruska[102], allowed him to observe two layers in the fibre section: a compact outer layer consisting of fibrils, and a porous inner layer. Later work attempted to identify the structural units into which the fibres break down when disintegrated[103]. X-ray diffraction[104,105] was often used in this work to complement electron microscopy; electron diffraction[106–108] was sometimes employed. Fibrillar structures were invariably observed in electron microscopic studies of cellulose, irrespective of the method of preparation. The width of the microfibril, as measured on the electron micrograph, is invariably between 60 and 200 Å, depending on the object and on the method of preparation. Cellulose filaments of 60 Å dimensions have been termed micellar[109]. After the technique of shadowing the object by vacuum evaporation of heavy metals had been proposed, a large number of papers on the electron microscopy of cellulose appeared. The fibrillar structure of the fibres was much more clearly demonstrated in this later work[75,110]. A model of the cellulose fibre was constructed with the help of X-ray diffraction studies.

The model proposed by Hess and Kissig involves alternate ordered and amorphous regions in the fibre. The microfibrils observed in the electron microscope could not be reconciled with this model. Hence, the objective of electron microscopic studies became to identify the structure of the microfibrils—the first structural units of cellulose fibres.

However, problems of contrast arose immediately when the structure of the individual microfibril (20–60 Å thick) was investigated. Since the thickness of the cellulose microfibril is near the lower limit of the condition for minimal contrast, a search for methods of enhancing the

contrast of the object began. Shadowing could not solve the problem, because it can do no more than outline the shape of the object and the relief of its surface, and furthermore it obscures the internal structure. Also, the grain size of the shadowing material varies between 15 and 50 Å, which imposes a further limitation on the development of fine detail. The first attempts to introduce contrast intensification into the electron microscopy of cellulose are due to Hess and coworkers[74,111,112]. Their work on poly(vinyl alcohol) established the possibility of impregnating oriented polymers with iodine. Iodine treatment was applied by Hess also to cellulose. Elongated cellulose fibres were treated with potassium iodide solution, dispersed, and examined in the electron microscope. The principle of this method depends on the unequal absorption

Figure 7. Dispersed cellulose fibres:
a) stained with iodine[74]; *b*) negative contrast obtained with the potassium salt of TPA[113].

of the contrast producing agent by the different portions of the fibre. Contrast was obtained by impregnating the object with iodine and with thallium. The work was aimed mainly at the application of the method to cellulose fibres, that is, at finding the conditions which control the sorption of iodine. Iodine was sorbed by the fibre in amounts corresponding to 12% by weight of the fibre. At this level of absorption, the X-ray diffraction patterns of the iodised fibre were indistinguishable from those of cellulose. The authors showed that, when thallium atoms are used to increase the contrast, the absorption should not exceed 6–8% of the weight of the fibre in order not to disrupt the structure. Thus, Hess's work on the structure of iodine-treated cellulose deals at the same time with the problem of the effect of the contrast material on the object being examined.

The electron micrographs of cellulose fibres treated as above (Fig. 7*a*) show very clearly, along the microfibrils, alternating dark and light transverse bands with repeat distances of 60–200 Å (small spacings) and 500–800 Å (large spacings). The authors examined various types of cellulose (ramie, Fortisan [rayon]) and the pictures were always identical. The ordered regions were invariably unaffected by the sorption of iodine, as shown by high-angle X-ray diffraction.

On the basis of the electron microscopic and X-ray diffraction results, Hess put forward a model of the elementary microfibril of cellulose. Ordered and disordered regions alternate periodically along the cellulose microfibril, and are separated by sharp boundaries, so that the ordered and the disordered regions of all fibrils occur at the same level. The thickness of the microfibril was 200–300 Å, and the micellar filaments (the thinnest of fibrils) were 60 Å wide. The latter value corresponded to the narrowest microfibrils observed after dispersion of the fibres with ultrasonic energy.

The fibrillar structure of cellulose is very clearly revealed in the electron micrographs when the specimen has been treated with the potassium salt of tungstophosphoric acid (TPA). A paper by Belavtseva and Tsvankin[113] describes an investigation of the structure of cellulose treated with TPA and its potassium salt, using high- and low-angle X-ray diffraction as well as electron microscopy. Special attention was paid to the effect of TPA and its salt on the structure of cellulose. The electron microscopic work with dispersed cellulose fibres led to the conclusion that after treatment with a 2% solution of TPA the contrast of the fibre is greatly enhanced, but the individual microfibril cannot be resolved. Treatment of the specimen with the potassium salt of TPA by the negative contrast intensification technique revealed individual microfibrils 70 Å wide and 500–2000 Å in length (Fig. 7*b*). In the photograph, dark regions are visible between fibrils: these are the potassium salt of TPA, which is deposited in the form of a chain of globules. The chain of contrast material had the same width and length as the microfibrils.

The difference between the electron micrographs obtained after treatment with TPA and with its potassium salt respectively, and also the influence of these materials on the structure of cellulose, could be explained by interpreting the X-ray diffraction results.

The high-angle diffraction patterns of the specimens were unaffected by treatment with the potassium salt of TPA, whereas if the specimen had been treated with TPA itself a strong background of the gaseous type appeared on the diffraction patterns. The position and texture of the reflections remained unchanged. These facts suggest that TPA molecules can penetrate into the pores but not into the ordered regions.

As has been previously established, the low-angle scattering of untreated fibres of cellulose arises from diffraction at the elongated pores, oriented along the texture axis[114]. The length of these pores is much greater than their cross-section, and therefore the scattering is concentrated at the equator of the diffraction pattern. Treatment with TPA and its potassium salt yielded different low-angle diffraction patterns. Fibres treated with TPA showed strong equatorial scattering, but after treatment with the potassium salt of TPA the scattering was almost isotropic. Calculations show that the strong scattering in the low-angle diffraction picture after treatment with TPA arises from diffraction at regions having an average cross-section of 30–50 Å, distributed in the form of elongated cylinders 400 Å in length: in other words, the TPA here is lodged in the pores in the form of cylinders. On the other hand, low-angle diffraction from fibres treated with the potassium salt of TPA leads to the conclusion that the TPA is present in the fibre as globules of ellipsoidal shape with axes 60 and 80 Å long. Thus, whereas low-angle scattering in the original fibre was due to density differences between the fibre and the pores, which are minimal, after treatment with TPA the pores are filled with the reagent, giving rise to the observed strong scattering. The authors

showed that when the specimen is treated with TPA (but not with the potassium salt of TPA) the contrast-producing agent—TPA—is absorbed in large quantities. This follows from the electron microscopic and the diffraction results as well as from the gravimetric results. The large amount of TPA filling the pores of the fibre also produces a greatly enhanced contrast in the electron microscopic image of the fibre, but it makes the microfibrils invisible because their scattering power is much less than that of the contrast material. Hence, TPA "stains" the whole of the fibre without revealing its fine structure. The electron microscopic results and those obtained by X-ray diffraction show that when the fibre is washed in distilled water the original state of affairs (before treatment of the fibre) is restored. Only occasionally do crystallites of TPA remain stuck in the pores after washing, and these can easily be seen in electron micrographs obtained under dark-field conditions.

Figure 8. Ultra-thin section of cellulose, treated with silver hydrosol[118].

The ultra-thin section method has been increasingly applied in recent years, as an alternative to the dispersion method, in studies of cellulose fibres. In this method, image contrast is obtained as a result of differences in thickness between different areas of the section, and the fibrillar nature of the fibres has sometimes been revealed in this way[115-117]. Only a few papers have been published on the contrast intensification of ultra-thin cellulose sections. In a paper[117] on the treatment of cellulose fibres with OsO_4 and $AgNO_3$ solutions, it is shown that the dark particles in fibre sections are located on internal surfaces of the fibre.

Salyaev[118] studied sections of plant roots treated with Ag and Pt hydrosols. The electron micrographs of the root sections clearly show, in the thickness of the cell wall, silver particles filling submicroscopic spaces and thus decorating the interfibrillar spaces of the cell walls (Fig. 8).

In the present article we have discussed only the work aimed at contrast intensification in cellulose, and structural problems (as well as other electron microscopic investigations) have been ignored. For information on these topics the reader is referred to a monograph on the electron microscopy of cellulose[119] and to various other publications.

Collagen

Regular striations similar to those found in cellulose and in synthetic fibres have been observed also in a number of biological polymers (for example, collagen). The present review is concerned mainly with synthetic polymers, and therefore we shall deal, briefly, only with the work on collagen, because the electron microscopic results for this material are in keeping with those obtained by X-ray diffraction, and furthermore the electron micrographs show a remarkable similarity to those of oriented synthetic polymers.

The first X-ray diffraction studies of collagen fibres[122,123] revealed the presence of a periodicity of 830, 432, and 838 Å. In this work, attention was devoted to the effect of reprecipitation on the crystal structure of the fibres[121]. Bear[122] observed a periodicity of 640 Å in the low-angle diffraction pattern of air-dried collagen tissue. When these tissues were examined in the electron microscope after mechanical disintegration but without any artificial staining, transverse striations with a periodicity of 500–900 Å were observed. The contrast was evidently due to differences in thickness between the different regions of the fibre. The periodic striations in collagen fibres are easily visible even after shadowing, although they are not discernible in synthetic fibres shadowed with metals.

Figure 9. Collagen treated with TPA[124].

The spacing of 640 Å has been shown, by X-ray diffraction, to be common to all collagen fibres whatever their origin.

By applying contrast intensification to collagen fibres, the periodic striation has been more clearly revealed in the electron micrographs. Furthermore, the application of contrast has led to the discovery in collagen fibres not only of large spacings (Fig. 9), but also of sub-periods within the large period or spacing. As for synthetic and cellulose fibres, OsO_4 and TPA have been used as contrast materials for collagen fibres[124,125]. In that work, dispersed collagen fibres treated with OsO_4 or with a 2% solution of TPA were found in the electron microscope to consist of a thick network of fibrils with clearly developed striations. The repeat distance was approximately 700–1000 Å (large spacing), which was itself made up of a large number of bands

30 Å wide. Collagen fibres can be very effectively "stained" by contrast materials, even the small sub-periods becoming visible, whereas in synthetic fibres it is quite difficult to reveal even the large spacing.

Attempts have been made[126-129] to understand the chemistry of the interaction between TPA and collagen fibres. It has been suggested that polypeptide chains are responsible for the periodicity of the striations in the fibres: the TPA attaches itself to the amino-acid residues and therefore cannot be washed out with water. To confirm this hypothesis, photometric curves of the darkening of collagen fibres after contrast intensification with chromium and with TPA were presented: small bands (sub-periods) are observed only with preparations treated with TPA (not those treated with chromium). The small spacings (or sub-periods) in collagen fibres are thus ascribed to the presence of a chemical repeat distance along the fibre, such as would result from a regular alternation of atoms or groups, whereas no explanation could be put forward regarding the origin of the superperiods.

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The tendency of modern, quantitative electron microscopy is to exploit more fully the potentialities of the electron microscopic method. In particular, the image contrast is one of the limiting factors in quantitative electron microscopy. The papers presented at the Symposium on "Quantitative Investigations in Electron Microscopy"[130] discuss the possibilities and prospects in this area.

For this reason, recent publications have been concerned with problems of contrast and contrast intensification. In a number of instances, morphological and structural problems in crystalline polymers have been solved by diffraction methods[131]. However, polymeric materials of low scattering power usually need additional treatment aimed at increasing the contrast. We may conclude, from this review of work on contrast intensification in synthetic polymers, that the problem is still far from solved. Only the following methods for enhancing the contrast of a polymeric specimen are known: shadowing, enhancing the ordered regions, negative contrast intensification, decoration, and contrast intensification by the reduction of silver ions. However, with the exception of shadowing, these procedures have been applied to polymers on a very modest scale as compared with the extensive application of a variety of contrast methods in biology. This is because the scientific applications of electron microscopy have so far been mainly in the field of biology. Furthermore, the specific properties of biological objects are more compatible with the full exploitation of contrast intensification. With synthetic polymers, contrast intensification presents some real difficulties, and in most cases the choice of contrast agent must be made by *ad hoc* methods.

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Water as a Semiconductor

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1. ANALOGY BETWEEN SEMICONDUCTORS AND AQUEOUS SOLUTIONS OF ELECTROLYTES

Over 10 years ago, Reiss and Fuller[1,2] drew attention to the qualitative similarity between electronic semiconductors (such as germanium) and solutions of electrolytes, and suggested a chemical approach to a better understanding of physicochemical phenomena in semiconducting crystals. Later, this concept was successfully applied to the discussion of chemical equilibrium and of impurity and defect interactions in crystalline semiconductors[3,4].

The principle of this analogy is that both water and germanium provide a dielectric medium for the motion and the interaction of charged particles. Water has an electrical conductivity due to its dissociation into H^+ and OH^- ions, the product of the concentrations of these ions remaining constant at a given temperature:

$$[H^+] \cdot [OH^-] = K_w . \quad (1)$$

This relationship is the exact analogue of the expression for the product of the concentrations of holes and electrons in an intrinsic semiconductor:

$$n \cdot p = n_i^2 = K_i . \quad (2)$$

Since both K_w and K_i are equilibrium constants, depending only on the temperature, the dissociation energy at constant pressure can be calculated from the van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} . \quad (3)$$

This energy amounts to 13.5 kcal mole^{-1} or 0.59 eV per molecule for water, and to ~ 15.7 kcal mole^{-1} or 0.68 eV per bond for germanium. The ionisation energy of germanium or silicon atoms defines the width of the forbidden band in these semiconductors.

The phase transformations which water undergoes, and also other, more complex phenomena, set a limit to the validity of this analogy. In any case, ΔH^0 is slightly dependent on T, leading to departures from linearity. In the case of semiconductors the effect manifests itself as a temperature dependence of the width of the forbidden band.

Expressions (1) and (2) apply not only to the dissociation of the pure materials, but also in the presence of ionised impurities, when the concentrations of charge carriers of opposite signs are no longer equal. Addition of an acid to water raises the concentration of H^+ above the equilibrium value and at the same time lowers the concentration of OH^-, so that the value of K_w remains constant. The corresponding process in semiconductors is a decrease in the concentration of electrons following addition of an acceptor impurity (which raises the concentration of holes). Thus, the terms "n-type" and "p-type" conductivity become the analogues of the terms "basic" and "acidic". We note, in this connection, that the concept of the "Fermi level", of fundamental importance in semiconductor physics, is identical to the electrochemical potential or partial molar free energy of the electron gas per electron[5]. Hence, the height of the Fermi level in the forbidden gap becomes analogous to the pH of an aqueous solution. When the Fermi level is located in the upper half of the forbidden band the system corresponds to a "basic" solution, and when the Fermi level is in the lower half of the borbidden band it corresponds to an "acidic" solution. In this sense, neutralisation of an acid by a base or dissolution in water of the salt of a strong base (e.g. KCl) is analogous to the compensation of an acceptor by a donor impurity.

The ionisation energies of donors and acceptors in semiconductors are comparable to the ionisation energies of weak bases and weak acids.

It has been pointed out[4] that the entropy factor ΔS_i^0 can be negative for weak electrolytes, whereas no entropy change has been reported for current carriers in semiconductors. Nevertheless, the ionisation energies of many weak acids lie in the same range as the ionisation energies of many acceptors in germanium (0.01–0.1 eV).

For example, the ionisation energy (or heat of dissociation for the following equilibria can be determined by means of Eqn. (3):

$$B \rightleftarrows B^- + e^+ \text{ (in the silicon lattice)}$$
$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \text{ (in aqueous solution)} ,$$

The values obtained are, respectively,

$$\Delta H^0_{CH_3COOH} = 4000 \text{ cal} = 0.17 \text{ eV}$$
$$\Delta H^0_B = 100 \text{ cal} = 0.043 \text{ eV}$$
(at room temperature) .

The fraction of donors or acceptors which are ionised depends on the position of the Fermi level, just as the degree of ionisation of a weak base or a weak acid depends on the pH of the solution.

Multiply ionised solutes, and also amphoteric solutes, are found both in aqueous and in semiconductor solutions. The dissociation of zinc hydroxide can be taken as an example of an amphoteric electrolyte in aqueous solutions.

Zinc hydroxide dissociates as a base when the pH of the medium is low, and as an acid when present in solutions of high pH:[6]

$$Zn(OH)_2 \xrightleftharpoons{\text{acidic medium}} ZnOH^+ + OH^-$$
$$H_2ZnO_2 \xrightleftharpoons{\text{alkaline medium}} H^+ + HZnO_2^- .$$

In a similar way, atoms of gold, say, in germanium and in silicon ionise as acceptors or as donors depending on the position of the Fermi level[7,8].

Many other examples of the similarity between aqueous and semiconductor solutions can be given. The basic concepts of mobility, drift, and diffusion of charge carriers are applicable to electrolytes as well as to semiconductors, although large differences in the numerical values are often found. Thus, the mobility of the H^+ ion in water is approximately 10^6 times lower than the mobility of the electron in germanium. Some properties of germanium and of water are compared in the Table.

As Fuller points out, the analogy between electronic semiconductors and aqueous solutions of electrolytes breaks down when we consider that the ionised atoms of donor and acceptor impurities in semiconductor crystals are immobile, whereas the ions formed by the dissociation of acids and bases are freely mobile throughout the bulk of

the solution. Another difference is the fact that interstitial ions are absent in aqueous solutions[4] whereas they play a major role in the physics of semiconductor crystals.

However, the mobility difference of ionised impurities does not set an absolute limit to the analogy, bearing in mind the appreciable mobility of lithium ions in germanium and silicon at elevated temperatures. In many cases this

Comparison of related parameters in germanium and water*.

Germanium parameters	Germanium properties	Water parameters	Water properties
1. Charge carriers	Electrons, holes, mobile impurity ions (lithium)	1. Charge carriers	Proton, hydroxyl ion, mobile impurity ions
2. Concentration product of intrinsic charge carriers, at 25°C (atoms cm^{-3})^2	5.61×10^{26}	2. Ionic product of water at 25°C (ions cm^{-3})^2	3.6×10^{27}
3. Effective mass of the electron	Density-of-states mass $m_\alpha = 0.22$	3. Effective mass of the proton	1836
4. Mobility of charge carriers at 290°K, $cm^2\ V^{-1}\ s^{-1}$		4. Mobility of charge carriers at 293°K, $cm^2\ V^{-1}\ s^{-1}$	
electrons	3900 ± 100	protons	3.0×10^{-3}
holes	1900 ± 50	hydroxyl ions	1.7×10^{-3}
5. Ionisation energy of donors and acceptors (Groups III and V)	0.01–0.1 eV	5. Heat of dissociation of weak acids and bases	0.01–0.1 eV
6. Resistivity in the intrinsic region, ohm-cm, at 25°C	47	6. Resistivity of pure water, ohm-cm, at 25°C	20×10^6
7. Lifetime of non-equilibrium charge carriers, ms	2000	7. Lifetime of non-equilibrium ions, ms	6.6×10^{-6} 1.3×10^{-5}
8. Diffusion length of extrinsic charge carriers, cm	0.3	8. Diffusion length of extrinsic charge carriers, cm	2×10^{-8}

* This Table was assembled from published data [2,3,4,20,23].

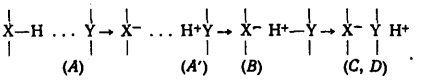
leads to the formation of donor–acceptor ion pairs, corresponding to the Debye–Hückel effect in electrolyte solutions. Furthermore, the acidic and basic residues in aqueous solutions can be spatially fixed in a high-polymer network, as is the case with the functional groups of ion-exchange resins and membranes[9].

2. THEORY OF PROTONIC SEMICONDUCTORS

The analogy between semiconductors and electrolyte solutions presented above is not a purely formal one. Studies of the physicochemical properties of water and of some other hydrogen-bonded substances have revealed that there are good reasons for classifying these materials as amorphous ionic semiconductors with a conductivity of the protonic type[10,11]. Shakhparonov[10,12,13] has introduced the concept of a protonic metallic bond, i.e. of a collective interaction between a proton gas and a system of negatively charged proton defects in whose field the proton gas is forced to move.

Shakhparonov bases his theory on a general proof that localised energy levels are converted into energy bands when charged particles interact in condensed systems[14].

His theory of protonic semiconductors offers a unified approach to the qualitative (and in many cases the quantitative) description of the basic features of dielectric polarisation and conductivity processes in water, alcohols, and many other substances with intermolecular hydrogen bonds. At the same time, the existing fund of experimental data on the temperature and frequency dependence of the dielectric constant can be used to refine the band structure model of protonic semiconductors. The energy spectrum of the states of a proton taking part in hydrogen bonding includes, in order of increasing energy, (a) a valence band, (b) an intermediate band in which states of the H_3O^+ type are formed, (c) levels associated with protonic excitons (exciprotons), (d) a conduction band. The energy band structure is shown schematically in Fig. 1. The change in energy state of a proton on being transferred from atom X to atom Y along the direction of the hydrogen bond (with simultaneous transfer from the valence to the conduction band) can be characterised by the following scheme



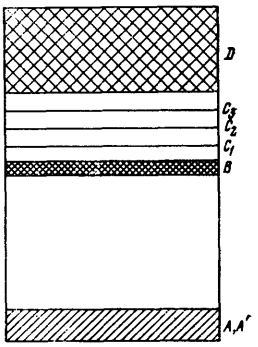


Figure 1. Energy level diagram for protonic semiconductors with intermolecular hydrogen bonds[13]:
A, A' valence band; B intermediate level; C_1, C_2 levels of proton excitons (exciprotons); D conduction band.

According to this scheme, both complex ions (such as H_3O^+) and free ions may be present in substances containing intermolecular hydrogen bonds. Transition from state A to state A' along the line of the hydrogen bond occurs by the tunnel effect with a frequency of the order of 10^{12}–10^{13} s^{-1}. The probabilities of finding a proton in states A and A' are approximately the same. Transition from A to B is accompanied by hydrogen bond breaking. There is evidence that this transition also can occur by the tunnel effect[15] provided the orientation of the molecules is favourable (i.e. when the donor atom is in direct contact with the acceptor atom). The contact may be broken (by thermal motion) at the instant when the proton is located on the acceptor atom, giving rise to the ions H_3O^+ and OH^- in water or ROH_2^+ and RO^- in alcohols, where R is a hydrocarbon radical. Unless the proton is immediately transferred from state B to state C after rupture of the intermolecular hydrogen bond, the ions HY^+ and X^- can readily recombine. Recombination can occur also by the tunnelling of a proton along the line of the intermolecular hydrogen bond. Hence, the lifetime of an H_3O^+ ion is only 10^{-13}–10^{-14} s. Transition from B to C, i.e. to any of the exciproton levels, leads to further expenditure of energy. The mutual repulsion of the protons in the H^+Y ion raises the energy of the proton. Therefore, the difference in potential energy of a proton in positions B and C may not be very large. This transition involves surmounting a potential

barrier whose free enthalpy of activation in the liquid phase usually amounts to 2–5 kcal mole^{-1} (i.e. 0.09–0.2 eV). Transition of a proton from C to D (i.e. to the conduction band) requires a small expenditure of energy of the order of $2kT$ and involves a change in the entropy of the system.

Upon entering the conduction band, protons acquire various properties not unlike the properties of electrons in electronic semiconductors. Protons and proton defects (the ions OH^-, RO^-, etc.) show an anomalously high mobility. The concentration of protons is an exponential function of $1/T$. Protons in the conduction band can be treated as a proton gas [16]. Hence there are grounds for assuming that some of the relationships derived in the band theory may apply also to protonic semiconductors. Since the mass of the proton is 1836 times that of the electron, the degeneracy condition [17] is not fulfilled in aqueous solutions:

$$kT_{deg} \simeq \frac{h^2}{8m^{(N)}} n_{deg}^{2/3} , \qquad (4)$$

where $m^{(N)}$ is the effective density-of-states mass of the charge carriers and n is their concentration. Hence, the proton gas in the conduction band is non-degenerate.

According to Shakhparonov [13], the methods of the band theory, developed for electronic semiconductors, can be used to a first approximation to treat the motion of protons and proton defects in the conduction band. The mobility of protons is found to be

$$\mu = \frac{e}{(m^*)^{1/2}} \left(\frac{m_0}{m_0 + m^*}\right)^{1/2} \frac{1}{2N_0 r_0^2 (2\pi kT)^{1/2} Y(\rho,T)} , \qquad (5)$$

where N_0 is the number of neutral molecules in 1 cm^3, m_0 and r_0 are the mass and the radius of the molecules, m^* is the effective mass of the protons, and $Y(\rho,T)$ is a semi-empirical Enskog function depending on the structure of the material as well as on the density ρ and the temperature T. Since the values of m^* and $Y(\rho,T)$ are not known, a quantitative test of the validity of Eqn. (5) cannot readily be made. However, it is possible to calculate the theoretical ratio of the mobility of hydrogen ions in water to that of deuterium ions in heavy water. The structure of D_2O is practically indistinguishable from the structure of H_2O. At the same temperature, the quantities N_0 and r_0 for H_2O and D_2O are identical. Assuming $m_D^*/m^* = 2$ and $Y_{D_2O} = Y_{H_2O}$ we obtain, from Eqn. (5), $\mu_H/\mu_D = 1.43$, which agrees exactly with the value found experimentally at 18°C.

3. SEMICONDUCTOR DEVICES BASED ON WATER

Various types of electrochemical transducers (or chemotrons) have been used successfully in technology for a number of years as rectifiers, stabilisers, logic cells, relays, d.c. and a.c. amplifiers, etc. [18]. The vast majority of these devices are not true analogues of semiconductor devices. However, many attempts have been made to realise devices of the diode or even the triode type using water as a semiconductor.

Fuller was the first to point out the analogy, in 1956, [2] between a p–n junction in a semiconductor and an electrochemical concentration cell. Fig. 2 shows a schematic comparison of the acid–base cell $H_2|HCl_{aq}|NaOH_{aq}|H_2$ with a semiconductor p–n junction. The ions H^+ and OH^- correspond to electrons and positive holes.

We had previously pointed out [9] that the junction between two ion-exchange membranes of opposite sign offers an even closer analogy to the junction between two semiconductors of opposite conductivity type, because the immobile, ionised, functional groups of the resin give rise to an electric field of the appropriate sign whilst the mobile ions of the electrolyte play the part of charge carriers (see Fig. 2). Independently, Bockris and coworkers [19] showed that the mobility of the counterions can be suppressed not only by using ion-exchange membranes with oppositely charged functional groups but also by separating aqueous solutions of high-molecular polyacids and polybases by a thin semipermeable membrane.

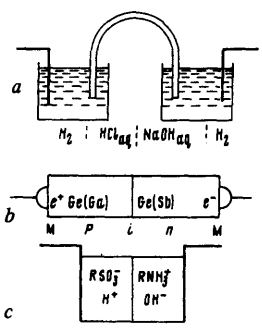


Figure 2. Analogy between (*a*) the acid–base concentration cell, (*b*) the p–n junction, and (*c*) the ion-exchange cell with membranes containing functional groups of opposite signs.

In either case, the application of an external electric field results in asymmetrical electrical conduction in the resin cell, i.e. in the rectification of electric current. Thus, when the cell is connected in the forward direction the mobile H^+ and OH^- ions move towards each other and recombine at the interface between the two membranes. In the blocking direction, the mobile charge carriers are drawn away from the interface, forming a region which is depleted of charge carriers and in which H^+ and OH^- ion pairs can arise only as a result of the termal dissociation of water—a relatively slow process.

A typical, static current–voltage characteristic for an ion-exchange resin rectifying cell, as published by many workers [19–21], is reproduced in Fig. 3. Its shape is reminiscent of a semiconductor diode characteristic, but it shows an additional hysteresis loop. This is ascribed to polarisation of the electrodes, the loop area being significantly decreased by the addition of depolarisers. The nature of the metal electrodes also plays a part [9]. Rectification coefficients do not usually exceed a value of 40. [9,21,22] The change in shape of a 50 Hz sine wave caused by the rectifying action of ion-exchange cells is illustrated in Fig. 4. A strong dependence of the rectification coefficient on frequency was noted in attempts to use cells of this type to rectify alternating current. Most authors [9,19] observed rectification up to frequencies not above 50–60 Hz, but Friedländer [22] reports an appreciable effect even at 6000 Hz. Seno and Yamabe [20] made a special study of this effect, and found that the rectification coefficient falls off rapidly above 1 Hz (Fig. 5), tending to zero above 1000 Hz.

According to the theory developed by Seno and Yamabe, the net current through the membrane cell is satisfactorily described by the expression

$$i = e\left(\frac{D_A n_A}{L_n} - \frac{D_m m_A}{L_m}\right)[\exp(eV/kT) - 1] , \qquad (6)$$

where the subscript n refers to protons and m to hydroxyl ions. L_n and D_n are the diffusion length and the diffusion

coefficient of protons in the region of the anionic resin, L_m and D_m are the corresponding quantities for hydroxyl ions; n_A and m_A are the concentrations of protons and hydroxyl ions in the anionic resin region.

Eqn. (6) is the analogue of Shockley's equation for a p–n junction in a semiconductor [23]. This suggests that the same rectification mechanism is operative in both systems,

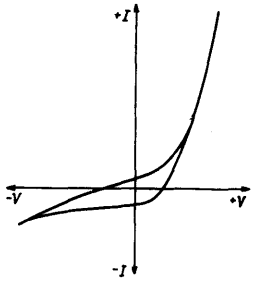


Figure 3. Typical current–voltage curve of an ion-exchange cell [21].

the cationic membrane corresponding to the n-type semiconductor and the anionic to the p-type. Thus, we conclude that a system in which the positive electrode is connected to the cationic exchange resin and the negative electrode is connected to the anion exchange resin will offer a higher resistance to direct current than a system of the opposite polarity.

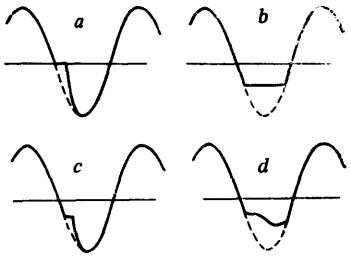


Figure 4. Change in shape of a current sine-wave at 50 Hz frequency resulting from rectification by ion-exchange cells [9]. *a*, *b*, *c*, and *d* are the characteristics of different ion-exchange cells.

Studies of the electrical characteristics of systems based on ion-exchange membranes of different polarities have not been confined to realising the simplest analogue of a semiconductor diode. Bockris and coworkers [19] obtained a rectification efficiency of 85% by connecting several membrane diodes in series.

Later workers [24] showed that the rectification efficiency for homogeneous membranes depends on the ratio of the concentration of fixed charges in the membrane to the concentration of ions in solution. The rectification effect shows a marked increase when this ratio is increased. In addition, the pore size has an important effect in the case of inhomogeneous membranes.

Lovreček and Kunst [25], in some later work on the membrane non-linear element, described an amplifier consisting of two cationic and two anionic membranes, shown diagrammatically in Fig. 6. A current I_i in the input circuit produces an excess current I_e in the main circuit:

$$I_e = I_m - (I_m^0 + I_i), \qquad (7)$$

where I_m is the effective current in the main circuit during the measurement period, I_m^0 is the effective current in the main circuit when this circuit alone is connected, and I_i is the effective current in the input circuit†.

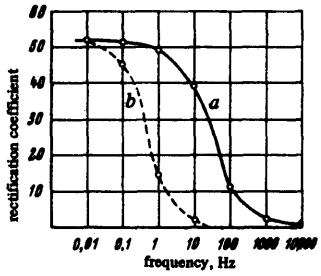


Figure 5. Frequency characteristic of an ion-exchange cell [20]: *a*) characteristic explored from reverse to forward current; *b*) from forward to reverse current.

The current amplification coefficient $P = I_e/I_i$, calculated as the ratio of the excess current to the current in the input circuit, can reach a value of 4. Current amplification is obtained because the current flowing in the input circuit produces injection of mobile ionic charge carriers in whichever diode is biassed in the blocking direction.

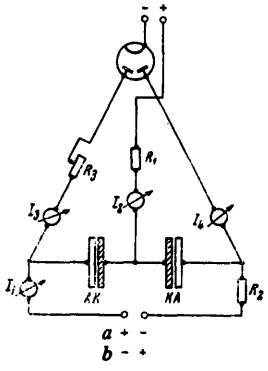


Figure 6. Circuit diagram of a current amplifier based on ion-exchange membranes [25,26].

As a result, the resistance of the diode drops and the current in the main circuit increases.

Lovreček and Kunst investigated also the variation of amplification with frequency and time [26], and they showed

† The currents I_m, I_m^0, and I_i are complex functions of the currents I_1, I_2, I_3, and I_4 shown in the circuit diagram of Fig.6.

that the amplification coefficient is decreased four or five-fold by changing the frequency from 50 to 2000 Hz.

In an attempt to carry the analogy between the membrane cell and the p-n junction a stage further, the Japanese workers Oshida and Yoshida [27,28] constructed a model of a photogalvanic cell. The cation exchange membrance in the H^+ form was saturated with the basic dye thionine in 5×10^{-5} M aqueous solution. The anion exchange membrane was immersed in a 5×10^{-3} M solution of ascorbic acid. (A mixture of thionine and ascorbic acid solutions is known to be bleached by the action of light.) Platinum gauze electrodes were pressed against the assembled membranes with Perspex plates. The cell was illuminated with a 150 W xenon lamp through a filter which absorbed infrared radiation. By measuring the electrical potential of the cell with and without illumination from the lamp, the growth and decay of a photo-e.m.f. was observed against the background of the gradually decreasing membrane potential of the cell. Photocurrents were very small (of the order of a few microamperes): this was ascribed, in particular, to the high internal resistance of the cell (3500 ohm). The power generated by the photogalvanic cell was 10^{-7} W.

4. PROSPECTS OF FURTHER WORK ON SEMICONDUCTOR DEVICES BASED ON WATER

The theory of protonic semiconductors is still in its initial stages of development. We still do not know how far the parallelism between the energy states of charge carriers in electronic semiconductors and in their protonic analogues may be taken. Theoretical studies, in depth, of the band model of protonic semiconductors are needed, because there must be substantial differences between the final expressions of the energy band theory for protonic and for electronic semiconductors respectively, despite the generality of the main starting premises.

The energy band model for protonic semiconductors considered here is only a first approximation. Thus, several intermediate levels or bands can be expected to arise in solutions containing several substances capable of forming hydrogen bonds [10].

Nothing appears to have been published on the band structure of aqueous solutions of electrolytes, which can obviously be considered as impurity protonic semiconductors in contrast to water—a protonic semiconductor with intrinsic conduction. The band theory of protonic semiconductors has not yet been developed to the stage where the parameters of devices based on these materials can be calculated and predicted theoretically.

Nevertheless, the results of the work reviewed here show unambiguously that the semiconductor properties of water can be exploited to realise analogues of a number of familiar devices—in particular, those relaying on the operation of p-n junctions. However, the low mobility of the charge carriers and the occurrence of electrochemical side-reactions at the electrodes introduce serious limitations on the frequency behaviour and other characteristics of devices based on ion-exchange membranes. As a result, these devices are hardly ever in a position to compete with their prototypes, based on electronic semiconductor materials. It should be noted that ion-exchange cells have also a number of favourable properties. For example, these cells can be used to construct models of processes occurring at p-n junctions [9], thanks to the simplicity of assembly and to the lack of critical requirements on size and geometrical shape. Radiation, also, is known to have very little effect on the dissociation and structure of water, and therefore ion-exchange devices can be expected to have a high radiation stability [2]. In principle, ion-exchange devices, like chemotrons, are capable of operation at elevated temperatures, of the order of 500°C and higher, if the electrolyte solutions are replaced by fused salts [18]. In contrast to electronic semiconductors, the difference in chemical nature of the charge carriers and the ability (in principle) to choose systems in which chemical interaction of the components produces both carrier recombination and carrier generation can lead to the realisation of new types of device quite unlike any of the devices based on electronic semiconductors.

We note also that the interest which has been shown in semiconductor devices based on water stems largely from the realisation of the outstanding role played by semiconducting membranes in the operation of the functions of nerve cells (neurons) [17]. Neurophysiological investigations have shown that the propagation of the nerve impulse and the transmission of the impulse from one axon to the next can probably be explained in terms of the rectification which occurs at junctions between cation and anion exchange membranes [21,29,30] present in the cell walls. It follows that the development and study of characteristic active elements based on water may prove to be a path to the realisation of logic cells of the neuristor type and of complex biological models of the "artificial brain" type.

Undoubtedly, the most interesting problem posed by the study and the practical application of the semiconductor properties of water, a problem straddling the boundary of physics, chemistry, semiconductor technology, and biology, will prove to be the object of intensive theoretical and experimental research in the next few years.

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Reactions of the Chlorides of Phosphorus Acids with Unsaturated Compounds

N.A.Pudovik and V.K.Khairullin

The review deals with the reactions of the chlorides of acids derived from trivalent and tetravalent phosphorus with unsaturated compounds. Apart from their theoretical importance, these reactions are of great practical interest, since with their aid it is possible to obtain a wide variety of new and interesting types of organophosphorus compounds. In the first part of the review the addition reactions of various halides of trivalent phosphorus acids to ethylene and diene hydrocarbons, $\alpha\beta$-unsaturated aldehydes, ketones, and acids are considered, as well as the oxidative chlorophosphination of unsaturated compounds. The second part of the review is devoted to the reactions of the chlorides of pentavalent phosphorus acids with ethylenic, acetylenic, and diene hydrocarbons and with vinyl ethers and esters and also the addition reactions of dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides.

CONTENTS

I. Introduction 317
II. Reactions of the chlorides of trivalent and pentavalent phosphorus acids with unsaturated compounds 318
1. Addition of phosphorus trichloride and tribromide to alkenes 318
2. Addition of the chlorides of phosphorus(III) acids to hydrocarbons with conjugated double bonds 318
3. Addition of the chlorides of phosphorus(III) acids to $\alpha\beta$-unsaturated aldehydes and ketones 321
4. Addition of the chlorides of phosphorus(III) acids to $\alpha\beta$-unsaturated carboxylic acids 323
5. Oxidative chlorophosphination of unsaturated compounds 324
III. Reactions of the chlorides of phosphorus(V) acids with unsaturated compounds 325
1. Reactions of the chlorides of phosphorus(V) acids with alkenes 325
2. Reactions of phosphorus pentachloride with hydrocarbons containing a conjugated system of double and triple bonds 326
3. Reactions of the chlorides of phosphorus(V) acids with vinyl ethers 327
4. Reactions of phosphorus pentachloride with enol esters 328
5. Addition of dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides to unsaturated compounds 329

I. INTRODUCTION

Apart from the widely known substitution reactions of the halides of trivalent and pentavalent phosphorus in which halogen atoms are exchanged for a hydroxy-group, a carbonyl oxygen, or any organic residue, the reactions involving their addition to unsaturated compounds are assuming increasing importance. In addition to their theoretical value these reactions are also of great practical interest, since with their aid it is possible to prepare a wide variety of new and interesting types of organophosphorus compounds. Until recently the range of addition

reactions investigated was fairly narrow and included mainly ethylenic and acetylenic hydrocarbons and unsaturated ketones. These and other addition reactions of phosphorus halides (reactions with epoxides and carbonyl compounds) were reviewed in 1947 by M. I. Kabachnik. During the past two decades the addition reactions of phosphorus halides to unsaturated compounds have been studied very vigorously; apart from the development of earlier studies, a number of new very interesting reactions have been found, such as the addition of phosphorus(III) halides to compounds containing a conjugated system of double bonds and to unsaturated acids, oxidative chlorophosphination, reactions of phosphorus(V) halides with diene hydrocarbons and enol ethers and esters, and the addition reactions of dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides to unsaturated compounds. The majority of these reactions were discovered and developed by Soviet chemists.

Intensive study of reactions of this type is being continued at the present time and they include both new types of phosphorus halides and of unsaturated compounds. Definite advances have also been made in the study of the mechanism of certain reactions.

We believe it is interesting and timely to compile these extensive and interesting data on the addition reactions of trivalent and pentavalent phosphorus to unsaturated compounds which have accumulated during twenty years. In the review we did not consider the earlier studies which have been summarised by Kabachnik with the exception of those few cases where this was necessary either for the explanation of the systematic development of studies on definite problems or for the examination of the mechanism of certain reactions.

II. REACTIONS OF THE CHLORIDES OF TRIVALENT AND PENTAVALENT PHOSPHORUS ACIDS WITH UNSATURATED COMPOUNDS

1. Addition of phosphorus trichloride and tribromide to alkenes

Under the usual conditions phosphorus trihalides do not add to alkenes. In 1945 Kharasch and coworkers[1,2] described for the first time a process of this kind in the presence of free radicals in the reaction medium. The radicals were generated by the thermal decomposition of acetyl peroxide introduced into the reaction:

$$(CH_3COO)_2 \rightarrow \dot{C}H_3 + CO_2 + CH_3C\dot{O}O,$$
$$\dot{C}H_3 + PCl_3 \rightarrow CH_3Cl + \dot{P}Cl_2,$$
$$RCH{=}CH_2 + \dot{P}Cl_2 \rightarrow R\dot{C}H{-}CH_2PCl_2,$$
$$R\dot{C}H{-}CH_2PCl_2 + PCl_3 \rightarrow RCHCl{-}CH_2PCl_2 + \dot{P}Cl_2 \text{ etc.}$$

The chain reaction results in the formation of chloroalkyldichlorophosphines. The main addition reaction is accompanied by a telomerisation reaction which leads to high-boiling products:

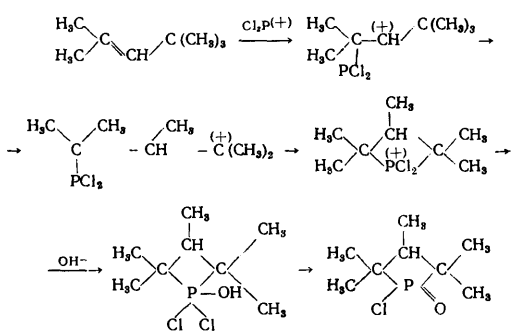
$$R\dot{C}H{-}CH_2PCl_2 + RCH{=}CH_2 \rightarrow R\dot{C}H{-}CH_2{-}CHR{-}CH_2PCl_2,$$
$$R\dot{C}H{-}CH_2{-}CHR{-}CH_2PCl_2 + PCl_3 \rightarrow RCHCl{-}CH_2{-}CHR{-}CH_2PCl_2 + Cl_2\dot{P}.$$

Reactions involving the addition of phosphorus trihalides to a double carbon–carbon bond can be initiated by ultraviolet radiation[3]. When phosphorus tribromide reacts with ethylene under the usual conditions, β-bromoethyldibromophosphine forms in 14% yield; when the reaction temperature is raised to 150°C, the yield increases to 40%. A mixture of isomers is formed with asymmetric olefins, this being confirmed by NMR spectra and gas chromatography. The authors of these investigations suggest that $Br^{\bullet}$ and $Br_2P^{\bullet}$ radicals participate in the reaction:

$$PBr_3 \xrightarrow{h\nu} Br^{\bullet} + Br_2P^{\bullet},$$
$$Br^{\bullet} + CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}\dot{C}H{-}CH_2Br,$$
$$CH_3{-}\dot{C}H{-}CH_2Br + PBr_3 \rightleftarrows CH_3{-}CH(\dot{P}Br_3){-}CH_2Br,$$
$$CH_3{-}CH(\dot{P}Br_3){-}CH_2Br + CH_3CH{=}CH_2 \rightarrow CH_3{-}CH(PBr_2)CH_2Br + CH_3{-}\dot{C}H{-}CH_2Br,$$
$$Br_2\dot{P} + CH_3{-}CH{=}CH_2 \rightarrow CH_3\dot{C}H{-}CH_2PBr_2,$$
$$CH_3\dot{C}H{-}CH_2PBr_2 + PBr_3 \rightarrow CH_3{-}CHBr{-}CH_2PBr_2 + Br_2P^{\bullet}.$$

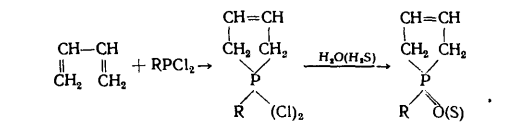
The first type of reaction takes place preferentially. A similar mechanism has been proposed by Little and coworkers[4,5] for reactions involving the addition of phosphorus trichloride to asymmetric olefins under the action of ultraviolet radiation. Trivedi's data[6] concerning the presence of a number of special absorption bands in the spectrum of phosphorus trichloride exposed to ultraviolet radiation confirm this mechanism (involving the participation of $Cl^{\bullet}$ and $Cl_2P^{\bullet}$ radicals).

Phosphorus trichloride adds to olefins in the presence of aluminium trichloride[7–10]. The intermediate complexes are decomposed by methanol and water. According to NMR spectroscopic data the phosphorus-containing acids formed have a cyclic structure. It is suggested (but it has not been confirmed experimentally so far) that reactions of this type involve an ionic mechanism with formation in the first stage of the $Cl_2P^{(+)}$ cation, for example in the case of 2,2,4-trimethylpent-2-ene we have



2. Addition of the Chlorides of Phosphorus(III) Acids to Hydrocarbons with Conjugated Double Bonds

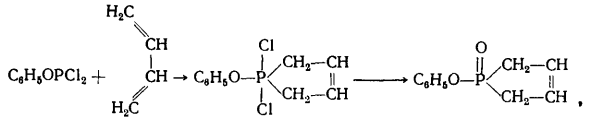
In 1953 McCormack[11,12] found that alkyl-(or aryl-)dichloro-(or dibromo-)phosphines add to diene hydrocarbons with formation of phosphorus-containing cyclic compounds—derivatives of *PP*-dihalogeno-1-phosphacyclopent-3-ene. On their decomposition with water or hydrogen sulphide, 1-oxo- or 1-thiono-phosphacyclopentenes were obtained:



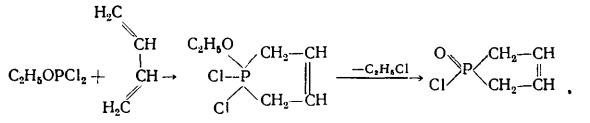
These interesting studies underwent considerable development in subsequent years.

Arbuzov and Shapshińskaya[13,14,15] investigated the addition of aryldichlorophosphines to various diene hydrocarbons. They suggested a reaction mechanism and obtained compounds of the 1-oxo-1-phosphacyclopentene series hitherto not described in the literature. They discovered

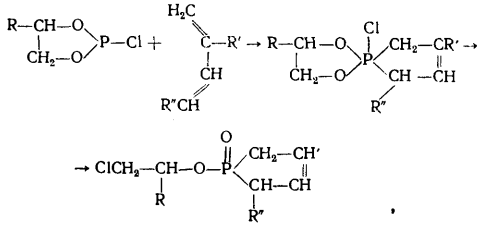
for the first time the reaction of phenyl and ethyl phosphorodichloridites with diene hydrocarbons. Phenyl phosphorodichloridite reacts without the Arbuzov arrangement



while the reaction of ethyl phosphorodichloridite does involve the rearrangement with elimination of alkyl halide:



At the same time Petrov and Razumova[16] studied the reaction of the glycol esters of phosphorochloridous acid with diene hydrocarbons (the final structure of the adducts is not quoted) and obtained the esters of the oxaphospholene oxide series[17]:

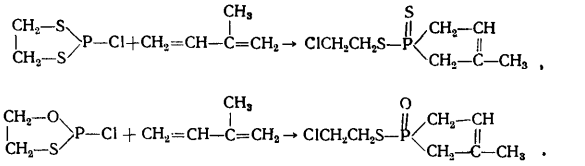


where (1) R = R′ = R″ = H, (2) R = R″ = H and R″ = CH_3, (3) R = CH_3 and R′ = R″ = H, (4) R = R′ = CH_3 and R″ = H, (5) R = R″ = CH_3 and R′ = H, and (6) R = CH_3, R′ = Cl, and R″ = H. They demonstrated the structure of their products by nuclear and proton magnetic resonance and infrared spectroscopy and chemically. A mechanism was suggested for this reaction, involving the Arbuzov rearrangement without the elimination of alkyl halide. When the catechol ester of phosphorochloridous acid is condensed with dienes, the Arbuzov rearrangement does not take place and the reaction terminates at the addition stage, evidently because of the stable bond between the oxygen and the carbon of the aromatic ring[18].

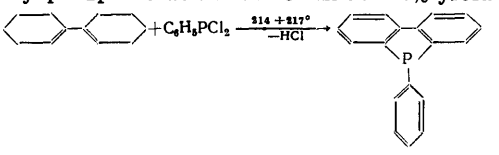
Arbuzov et al.[19,20] showed that cyclic phosphorochloridites add to various dienes with a conjugated system of double bonds by a 1,4-addition mechanism. Since in these reactions the cyclic phosphorochloridites behave as electron-donor components, the ease of the addition is determined by the electron-donor properties of the dienes. The latter become less pronounced in the series cyclopentadiene > anthracene > dicyclohexenyl > diisopropenyl > cyclohexadiene > divinyl > tetracyclone > hexachlorocyclopentadiene. Phosphorochloridites react at the highest rates with dienes at the end of the series and do not react with those pronounced electron-donor properties.

Subsequently Petrov and Razumova[21] showed that cyclic six-membered glycol esters of phosphorochloridous acid react with divinyl, isoprene, and diisopropenyl similarly as the corresponding esters with a five-membered ring. The products are 3-(γ-chloroalkoxy)phospholen 1-oxides. It has been established that in the Arbuzov rearrangement the ester ring is ruptured at the primary carbon atom.

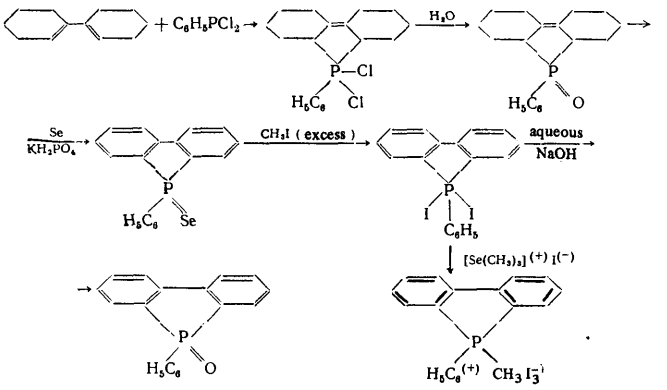
The reactions of the cyclic esters of phosphorochloridothious and phosphorochloridodithious acids with diene hydrocarbons take place similarly as those of their oxygen analogues[22]:



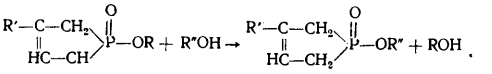
The adducts of dienes with halogen-containing derivatives of trivalent phosphorus can undergo a wide variety of very interesting reactions: for example when the adduct of dicyclohexenyl and phenyldichlorophosphine was heated, the tertiary phosphine was obtained in 50–60% yield[23,24]:



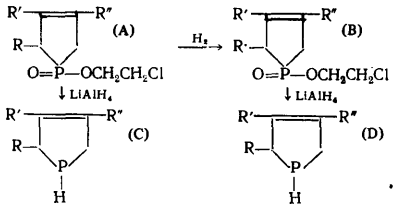
In the presence of selenium and the monopotassium salt of phosphoric acid, cyclic phosphine oxides are dehydrogenated, the oxygen bound to phosphorus being replaced by selenium:



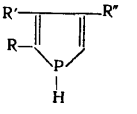
Alkoxyoxophosphacyclopentenes readily undergo transesterification with alcohols in the presence of potassium hydroxide[25]:



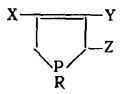
In the catalytic hydrogenation of phosphacyclopentene derivatives (A), compounds with the phospholan ring (B) were obtained[26]. When the esters (A and B) are reduced with lithium aluminium hydride, the phospholenes (C) and (D) are formed:



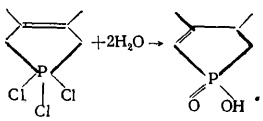
Phospholes can be obtained from these products by halogenation and dehydrohalogenation[27]:



The above syntheses of ring compounds containing phosphorus are simpler and more convenient than those already described in the literature[28]. When the adducts of methyl- or phenyl-dichlorophosphines with various dienes are reduced with magnesium in tetrahydrofuran solution, phospholens are obtained[29]:

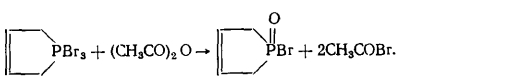


The results of studies on the hydrolysis and alcoholysis of the adducts of phosphorus trihalides with dienes are interesting. In the reaction of phosphorus trichloride and tribromide with divinyl, isoprene, diisopropenyl, dicyclohexene, and 1-phenylbuta-1,3-diene, Hasserodt et al.[30] and Weikamp and Korte[31] obtained the corresponding derivatives of 1,1,1-trihalogenophosphapentene. The authors showed by NMR and infrared spectroscopy that the hydrolysis and alcoholysis of 1,1,1-trichlorophosphapentene takes place with the migration of the double bond in the ring from position 3, 4 to position 2, 3:

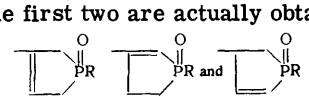


In the study of the reactions of 1,1,1-trichlorophosphapentene[30,31], a wide variety of derivatives of 1-hydroxy-1-oxo-1-phosphapent-2-enes were obtained.

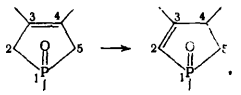
Arbuzov and Vizel'[32,33] isolated 1,1,1-trihalogenocyclopentenes in a pure form. Phosphorus tribromide reacts with diene hydrocarbons more vigorously than phosphorus trichloride. When the adducts of dienes with phosphorus tribromide are treated with acetic anhydride, the bromides of cyclic phosphinic acids are formed:



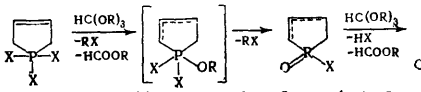
Their hydrolysis yields the acids and their reaction with alcohols the corresponding esters. In these reactions migration of the ring double bond was not observed. In subsequent studies of these investigators[34,35] it was shown that the lability of the double bond, its tendency to prototropic isomerisation, is a specific property of 1,1,1-trichlorophosphacyclopentene only. The migration of the double bond in this compound on hydrolysis, alcoholysis, or treatment with acetic anhydride occurs under very mild conditions. When 1,1,1-trichlorophosphacyclopentene is treated with sulphur dioxide, a mixture of isomeric 1-chloro-1-oxo-1-phosphacyclopentenes is formed. On the other hand, 1,1,1-tribromophosphacyclopentes do not show a tendency towards the migration of the double bond under similar conditions. This makes it possible to synthesise phosphacyclopentene derivatives with a specified position of the double bond in the ring. It has been shown by proton magnetic resonance spectroscopy and double nuclear magnetic resonance[35] that, of the three possible structures of phosphacyclopentene derivatives based on isoprene, only the first two are actually obtained:



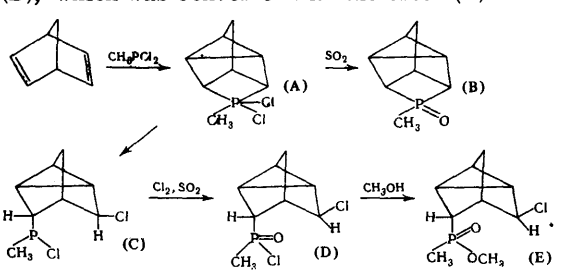
The position of the double bond depends not only on the nature of the halogen and the synthetic pathway but also on the nature of the diene and the symmetry of the distribution of the substituents in the ring. The position of the double bond can be demonstrated by NMR spectra. The application of NMR spectroscopy established that the migration of the double bond from position 3, 4 to position 2, 3 is accompanied by the displacement of one methyl group from the plane of the ring[33]:



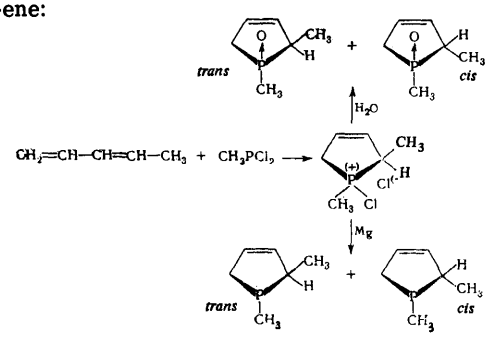
As a result, the phosphorus atom and C_4 become asymmetric. This behaviour is also observed in the reactions of 1,1,1-trihalogenophosphacyclopent-3-ene with orthoesters[36,37]:



When the reactant ratio is equimolar, 1-halogeno-1-oxophosphacyclopentenes are formed. When X = Br, the reaction takes place without migration of the double bond, the final product being 1-alkoxy-1-oxophosphacyclopent-3-ene. With chloro-derivatives, these reactions are accompanied by the migration of the double bond in the ring. Green[38] studied the addition of methyldichlorophosphine to bicyclo[2,2,1]heptadiene, a compound with isolated double bonds. The resulting crystalline adduct (A) yields the phosphine oxide (B) as a result of hydrolysis or under the action of sulphur dioxide. The structure of adduct (A), a substituted nortricyclene, was established by means of chemical conversions and by physical methods. Pyrolysis of the adduct gave the liquid isomer (C); its oxidation with chlorine and sulphur dioxide gave the acid chloride (D), which was converted into the ester (E):



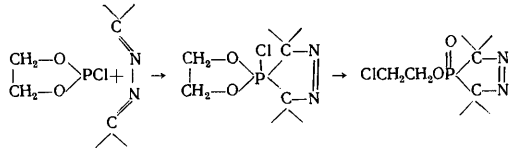
The stereochemistry of phosphacyclopentenes has been inadequately investigated so far. In the reaction of a mixture of the *cis*- and *trans*-forms of piperylene with methyldichlorophosphine followed by hydrolysis of the addition products, Quin and coworkers[39] obtained a mixture of the geometrical isomers of 1,2-dimethyl-1-oxophosphacyclopent-3-ene:



One isomer was isolated in a pure form by means of gas chromatography. The lack of migration of the double bond in the ring during hydrolysis in the suggested reaction mechanism is striking. Probably these reactions

require additional investigation. Reduction of the addition products with magnesium led to two stereoisomeric phosphines. When these are oxidised with hydrogen peroxide, the geometry of the molecules remains unaffected.

Not only hydrocarbons but also compounds with conjugated carbon–nitrogen double bonds can react with phosphorus(III) halides[40,41]. For example the reaction of cyclic phosphorochloridites with acetaldazine takes place by the following mechanism:



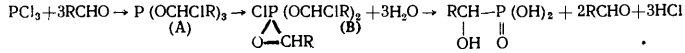
The structure of the products was confirmed by infrared and NMR spectroscopy.

The reactions of phosphorus(III) halides with diene systems open up wide possibilities for the preparation of a great variety of phosphocyclopentene derivatives and other organophosphorus compounds. Compounds of this type are of both theoretical and practical importance. Some of the phosphorus cyclopentene derivatives are recommended as catalysts for the preparation of carbodiimides and carbopolyimides[42,43].

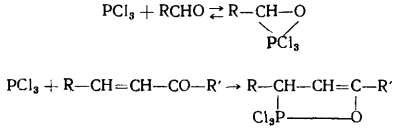
3. Addition of the Chlorides of Phosphorus(III) Acids to αβ-Unsaturated Aldehydes and Ketones

The study of this process was preceded by investigations of analogous reactions with saturated aldehydes and ketones. The results were subsequently used to account for the mechanism of reactions with both saturated and αβ-unsaturated carbonyl compounds; therefore it is useful to consider them briefly in the present review.

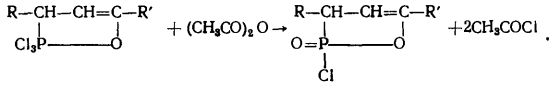
The first information about the reactions of aldehydes and ketones with phosphorus trichlorides is to be found in the work of Fossek[44–46] and Michaelis[47–51]. By hydrolysing the addition products, Fossek obtained a series of α-hydroxy-phosphonic acids. In the study of these reactions, Page[52] attempted to isolate the addition of products in a pure form by vacuum distillation, but his attempts failed because of the thermal instability of the products. After hydrolysis of the reaction products, he also isolated α-hydroxy-phosphonic acids. He suggested that the product of the addition of phosphorus trichloride to aldehydes formed initially is an ester of phosphorous acid (A), which subsequently rearranges to compound (B):



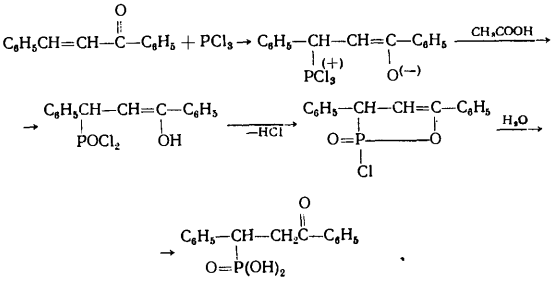
Thorough investigations of the addition of phosphorus trichlorides and certain other phosphorus(III) halides to saturated and unsaturated carbonyl compounds were begun in 1917 by Conant and coworkers[53–64]. In agreement with Michaelis' suggestions, Conant put forward the hypothesis of 1,2-addition of saturated aldehydes and ketones and 1,4-addition of αβ-unsaturated carbonyl compounds with formation of addition products containing three- and five-membered rings respectively:



The products were not isolated in a pure form; their hydrolysis yielded α-hydroxy-phosphonic or γ-oxo-phosphonic acid. Reaction with acetic anhydride gives rise to chlorides of cyclic acids with pentavalent phosphorus:

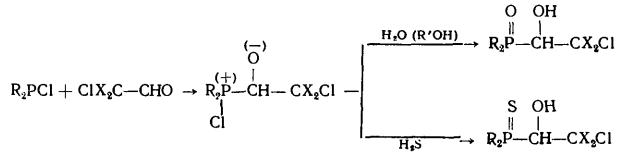


Subsequently, having carried out the reaction in glacial acetic acid, Conant and Wallingford[63] concluded that in the first stage a betaine-like addition product is formed, which is converted into a hydroxy- or oxo-phosphonic acid under the action of acetic acid and in subsequent hydrolysis. For example, for benzylideneacetophenene, these reactions can be described by the following mechanism:



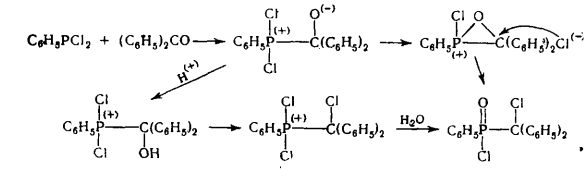
Evidently in this mechanism too the formation of a cyclic product is postulated, but only as a secondary reaction product. Conant's hypothesis concerning the formation in the reactions considered here of betaine-like, dipolar, and cyclic intermediates was widely used in subsequent investigations.

Tsivunin et al.[65], who studied the reactions of dialkyl- and diaryl-chlorophosphines with α-halogeno-aldehydes, suggest that in these reactions there is initial nucleophilic attack on the carbonyl carbon by the phosphorus atom with formation of an adduct in which the phosphorus is sp^3-hybridised. The subsequent decomposition of the complexes with water or alcohols leads to the formation of oxides of dialkyl- or diaryl-α-hydroxyethylphosphines. When the complexes are decomposed with hydrogen sulphide, the corresponding thiones are produced:

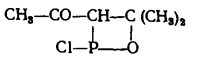


where R = C_2H_5 or C_6H_5 and X = H or Cl.

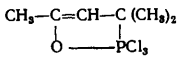
Freeman and Gallagher[66] studied the reaction of phenyldichlorophosphine with benzophenone in the presence of partially hydrated aluminium trichloride. This reaction gave a 65% yield of the chloride of (diphenylchloromethyl)-phenyl phosphinic acid. When the reaction is carried out in the presence of anhydrous aluminium trichloride, the yield of the acid chloride falls. The authors propose the following reaction mechanism:



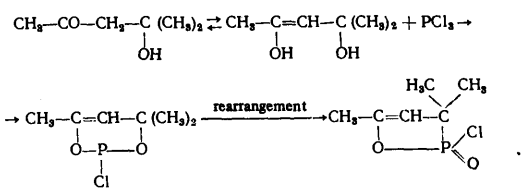
In 1884 Michaelis suggested that a cyclic intermediate, "diacetonephosphorus chloride", forms in the reaction between phosphorus trichloride and acetone in the presence of aluminium trichloride:



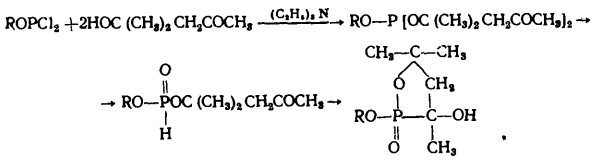
In their study of the reaction of phosphorus trichloride with mesityl oxide in the presence of acetic anhydride, Drake and Marvel[67] showed that 4-methylpentan-2-one-4-phosphonic acid forms as a result of the hydrolysis of the reaction product. On this basis, the following formula with a five-membered ring and pentavalent phosphorus was proposed for the "Michaelis chloride" (by analogy with Conant's views):



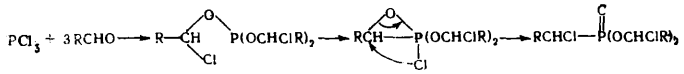
Anschutz et al.[68] and Michaelis[48] believed that diacetone alcohol formed initially and subsequently reacted with phosphorus trichloride to form the "Michaelis chloride":



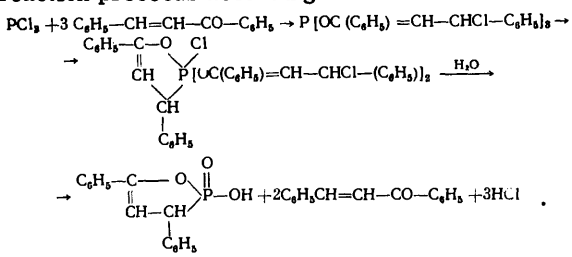
To confirm this mechanism, Anschutz carried out the reaction between phosphorus trichloride and diacetone alcohol. According to his data, the same "Michaelis chloride" is then formed. However, this hypothesis is probably incorrect, since Rizpolozhenskii[69] showed that esters of phosphorous acid are formed in the reaction between diacetone alcohol and monochlorides of phosphorus acids in the presence of a base. The reaction proceeds acccording to the following mechanism:



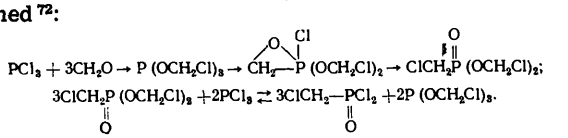
Kabachnik[70,71] believes that the mechanism proposed by Conant for the reaction between phosphorus halides and carbonyl compounds is unlikely because of the difficulty of the first stage, namely alkylation. He thinks that the more probable mechanism, very similar to the mechanism proposed by Page, is one consisting in the formation in the first reaction stage of a tri(α-halogeno-ester) of phosphorous acid, which subsequently undergoes the Arbuzov rearrangement to the ester of α-chloroalkylphosphonic acid:



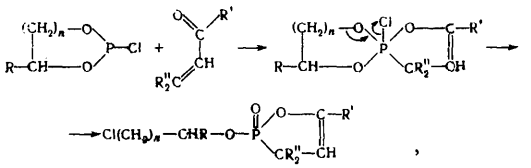
Hydrolysis of the α-chloroalkylphosphonic acid ester of the cyclic intermediate leads to the formation of the α-hydroxyalkylphosphonic acid. With unsaturated ketones, the reaction proceeds according to the mechanism



The validity of these mechanisms was confirmed for a number of examples. Thus in the reaction of phosphorus trichloride with paraformaldehyde in sealed tubes at 250°C, the dichloride of chloromethylphosphonic acid was obtained[72]:

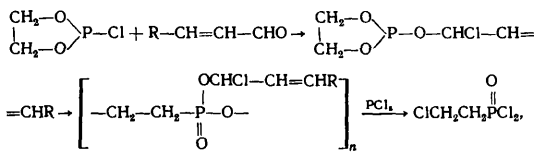


With benzaldehyde, the product was the dichloride of α-chlorobenzylphosphonic acid[73]. Kabachnik and Shepeleva[74] showed that these reactions are common to a wide range of aldehydes. Petrov and coworkers[39,40,75] demonstrated that the reaction of various glycol phosphorochloridites with methyl vinyl ketones or mesityl oxide involve 1,4-addition with subsequent Arbuzov rearrangement of the cyclic intermediate[75]:

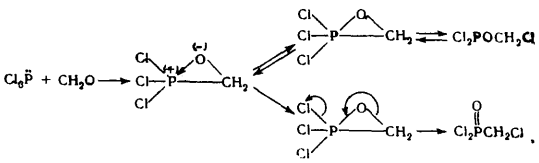


where n = 1 or 2, R = H or CH_3, R′ = CH_3, and R″ = H or CH_3.

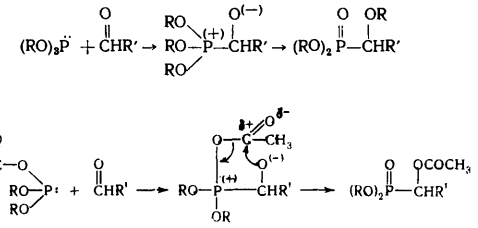
The structure of the final reaction products, isoxaphospholens, was demonstrated by infrared and nuclear and proton magnetic resonance spectroscopy. The reaction of glycol phosphorochloridite with acrolein and crotonic aldehydes leads to oligomeric products[40]. When these oligomers are treated with phosphorus pentachloride, the dichloride of β-chloroethylphosphonic acid is formed:



where R = H or CH_3. Probably the first stage of reactions of this type involves the attack by the nucleophilic phosphorus atom on the electrophilic carbon of the carbonyl group in the saturated aldehyde or the β-carbon atom in the unsaturated ketone. The dipolar ion produced cyclises with simultaneous migration of the P–C and O–C bonds, resulting in ring opening. Depending on the conditions, the rearrangement of the intermediate can lead to the formation of compounds with an ester of phosphorus–carbon bond:



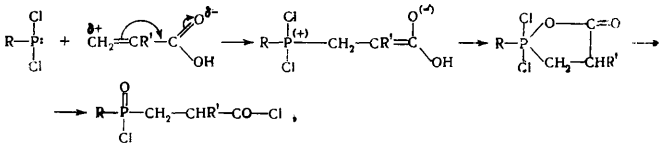
The validity of the suggested first reaction stage, the nucleophilic attack by the three-coordinated phosphorus atom, is confirmed by analogy with numerous reactions between carbonyl compounds and phosphites, which have been investigated in recent years [76]:



In the second reaction R′ can be an alkyl or a chloroalkyl group [77].

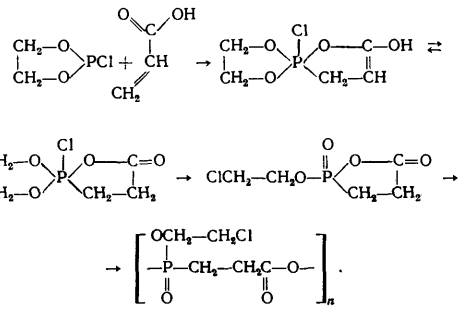
4. Addition of the Chlorides of Phosphorus(III) Acids to αβ-Unsaturated Carboxylic Acids

In 1964 one of the authors of the present review [78] found that, in the reaction between alkyl- or aryl-dichlorophosphines and αβ-unsaturated acids, the chlorides of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acid are formed in good yields:



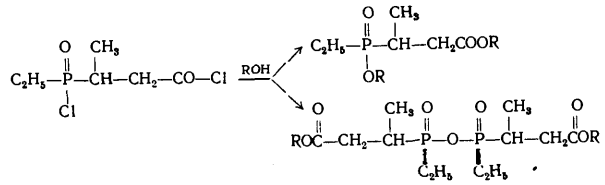
where R = CH_3, C_2H_5, C_6H_5, or C_7H_7 and R′ = H or CH_3.

According to the suggested reaction mechanism, the unshared pair of electrons of the three-coordinated phosphorus atom attacks the most electrophilic β-carbon atom of the αβ-unsaturated acid. The dipolar ion formed is converted into an adduct with a five-coordinated phosphorus atom, which undergoes the Arbuzov rearrangement to form the chloride of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acid [79,80]. In the same year Petrov and coworkers [39] pointed out the possibility of the reaction of glycol phosphorochloridites with acrylic and methacrylic acids. In the reaction between ethylene phosphorochloridite and acrylic acid [40], they obtained an oligomer:

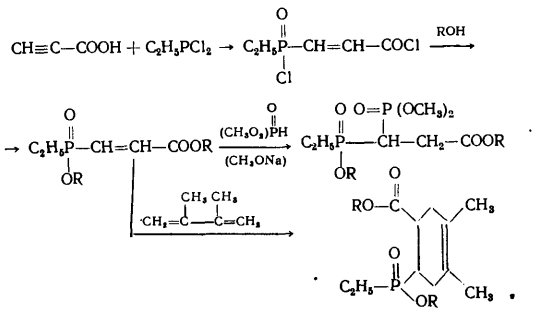


The structure of the oligomer was confirmed by infrared spectroscopy; when it was treated with phosphorus pentachloride, the chloride of dichlorophosphonopropionic acid was obtained.

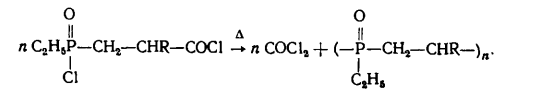
Continuing their investigation of this interesting reaction, the authors of the present review showed that the reaction of ethyldichlorophosphine with crotonic acid leads to the formation of the chloride of ethyl(β-chloroformyl-α-methylethyl)phosphinic acid in 78% yield [81]. When this acid chloride reacts with alcohols, anhydrides of ethyl(β-alkoxycarbonylisopropyl)phosphinic acid are formed together with the esters:



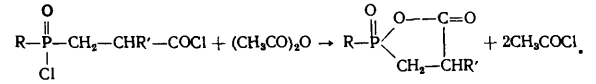
The chloride of ethyl(β-chloroformyl-α-methoxycarbonylethyl)phosphinic acid was obtained by the reaction of ethyldichlorophosphine with the monomethyl ester of maleic acid [82]. On the other hand, under the usual conditions maleic acid itself forms only maleic anhydride; when the reaction mixture is heated in sealed tubes, hydrogen chloride adds to the double bond of maleic anhydride. The reaction of ethyldichlorophosphine with pyromucic and cinnamic acids leads to the formation of considerable amounts of the chlorides of these acids. Evidently in these reactions the β-carbon atom of the acrylic system is blocked by substituents which reduce its positive charge. As a result, the reaction takes place mainly at the carbonyl group. Propiolic acid [83] reacts with ethyldichlorophosphine according to a mechanism similar to that for acrylic acid. The presence of the double bond in the resulting chloride of ethyl(β-chloroformylvinyl)phosphinic acid was confirmed by infrared spectroscopy, by its esterification with subsequent addition to the double bond of dimethyl phosphite esters, and by diene synthesis with 2,3-dimethylbutadiene:



In all cases the yields of the acid chlorides are fairly high when the reaction products are subjected to film distillation in a high vacuum (in the usual vacuum distillation the chlorides are extensively or completely decomposed with the evolution of phosgene and the formation of a polymer):



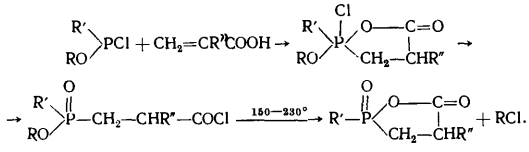
When acetic acid or acetic anhydride react with the chlorides of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acids, cyclic anhydrides are formed:



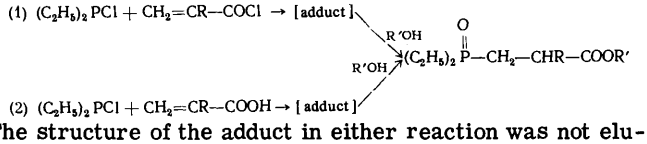
The P–O–C bond in these anhydrides is readily broken under the action of alcohols or amines.

In the reaction with acrylic acid, alkyl phosphorochloridites yield the chlorides of phosphono-carboxylic acids

[RO–P(O)–CH_2CH_2COCl] only when R is a chloro-substituted tertiary alkyl group. Phosphorochloridites with two tertiary chloro-substituted alkyl groups form with acrylic acid the chlorides of dialkylphosphinopropionic acid. Alkyl- or aryl-alkoxychlorophosphines react with $\alpha\beta$-unsaturated acids to form β-phosphono-carboxylic acids, which, on heating to 150–230°C, are converted into cyclic anhydrides with elimination of alkyl chloride:



Tsivunin et al.[85] showed that diethylchlorophosphine reacts with acrylic or methacrylic acid chlorides to form crystalline complexes, which, on treatment with an excess of alcohol, are converted into a dialkylphosphinylcarboxylic acid. The same esters were obtained by treating with alcohol complexes of diethylchlorophosphine with acrylic or methacrylic acids:



The structure of the adduct in either reaction was not elucidated but it is probably (in the second case) the oxide of diethyl(β-chloroformylalkyl)phosphine.

5. Oxidative Chlorophosphination of Unsaturated Compounds

One of the new very interesting and promising methods for the preparation of the dichlorides of alkyl- and chloroalkyl-phosphonic acids is oxidative chlorophosphination of saturated and unsaturated hydrocarbons and their various derivatives. This reaction was described almost simultaneously by Clayton and Jensen[86] in 1948 and by Soborovskii et al.[87] in 1949. (However, in his paper on the oxidative chlorophosphination of hydrocarbons, published in 1952, Graf[88] disputes the priority in the discovery, referring to the patent which he took out in 1942). The oxidative chlorophosphination of unsaturated hydrocarbons was first investigated by Soborovskii and coworkers[87].

The first step in the oxidative chlorophosphination of alkanes and alkenes is the addition of oxygen to phosphorus trichloride with formation of an adduct[88], which may be regarded as the biradical $Cl_3\dot{P}O\dot{O}$ [89,90] or the dipolar ion $Cl_3\overset{(+)}{P}O\overset{(-)}{O}$. In the absence of the hydrocarbon the adduct reacts with a second molecule of phosphorus trichloride, forming phosphorus oxychloride: $Cl_3\dot{P}O\dot{O} + PCl_3 \rightarrow 2POCl_3$. On the other hand, in the presence of the hydrocarbon the dichloride of alkyl- or chloroalkyl-phosphonic acid is formed as the final product:

$$Cl_3\dot{P}O\dot{O} + RH + PCl_3 \rightarrow RP(O)Cl_2 + POCl_3 + HCl,$$

$$Cl_3\dot{P}O\dot{O} + RCH{=}CH_2 + PCl_3 \rightarrow RC_2H_3Cl{-}P(O)Cl_2 + POCl_3.$$

The oxidative chlorophosphination of ethylene, propene, butene, and isobutene has been investigated[87]. When ethylene is used [with the molar ratio $PCl_3 : C_2H_4 = 1 : (3-15)$, at atmospheric pressure, and at a temperature between −140° and −110°C [91-94]], the dichloride of β-chloroethylphosphonic acid forms in yields of up to 80%. In this reaction the solvent may be methyl and ethyl chlorides, methylene chloride, carbon tetrachloride, chloroform, etc. When propene and butene are used in the reactions, a mixture of isomeric dichlorides of chloro-substituted alkylphosphonic acids, differing in the position of the chlorine atom and the $POCl_2$ group, is obtained[95]. There are two reasons for the formation of isomers in these reactions. There is a possibility of different sequences of addition of the chlorine atom and the $POCl_2$ group to the double bond of the olefin, or initially one of the hydrogen atoms of the methylene group is substituted by the $POCl_2$ group with subsequent addition of the resulting hydrogen chloride to the C=C bond. But-2-ene, which does not contain a methylene group, is an exception. Its oxidative chlorophosphination takes place only by the first pathway with formation of the dichloride of 2-chloro-1-methylpropylphosphonic acid. Despite the results of Isbell and Wadworth[96], Zinov'ev and Soborovskii[95] succeeded in isolating in the oxidative chlorophosphination of cyclohexene a mixture of isomeric dichlorides of chlorocyclohexylphosphonic acid. Apart from this mixture, the dichloride of cyclohexenylphosphonic acid formed, as a result of the elimination during distillation of hydrogen chloride from the dichlorides. The oxidative chlorophosphination of cyclohexane and cyclohexane was also studied by American workers[97]. The reactivity of cyclohexane proved to be higher by a factor of 2.3 than the reactivity of cyclohexane. The oxidative chlorophosphination of vinyl chloride, allyl chloride[98,99], 1,2-difluoroethylene, vinyl bromide, vinyl fluoride, 1,2-difluoroethylene, and vinylsulphonyl fluoride[100,101] takes place in most cases with formation of the dichlorides of dihalogeno-substituted alkylphosphonic acids. Their separation presents considerable difficulties but in some cases proved to be possible. Trichloroethylene and tetrachloroethylene do not enter into the oxidative chlorophosphination reaction. In the reaction with vinyl cyanide[102,103] a mixture of isomeric dichlorides of chlorocyanoethylphosphonic acids forms. In view of the impossibility of separating them by fractionation, they were converted into dimethyl esters. One of the esters proved to be liquid and the other crystalline. When oxygen was passed into a mixture of phosphorus trichloride and methyl acrylate[102], the dichloride of β-chloro-α-methoxycarbonylethylphosphonic acid was formed in high yield. In the dehydrochlorination of its esters with the aid of triethylamine, esters of α-alkoxycarbonylvinylphosphonic acid were obtained[104]. The dichloride of (triethylsilyl)chloroethylphosphinic acid was prepared in low yields by the oxidative chlorophosphination of triethylvinylsilane[105]. Acetylenic hydrocarbons react with phosphorus trichloride and oxygen without liberation of free hydrogen chloride[106]. The dichlorides of chloroalkenylphosphonic acids are then formed. The first member of the series (acetylene) reacts with the dichloride β-chlorovinylphosphonic acid to form the tetrachloride of dichloroethylenediphosphonic acid:

$$CH \equiv CH + 2PCl_3 + O_2 \rightarrow CHCl{=}CH{-}P(O)Cl_2 + POCl_3,$$

$$CHCl{=}CH{-}P(O)Cl_2 + 2PCl_3 + O_2 \rightarrow Cl_2\overset{O}{\overset{\|}{P}}{-}CHCl{-}CHCl{-}\overset{O}{\overset{\|}{P}}Cl_2.$$

The yields of the dichlorides, which are low for acetylene, increase for its homologues, hex-1-yne and phenylacetylene, reaching 24%. With vinylacetylene, the reaction takes place only at the triple bond:

$$CH_2{=}CH{-}C \equiv CH + 2PCl_3 + O_2 \rightarrow CH_2{=}CH{-}CCl{=}CH{-}P(O)Cl_2 + POCl_3.$$

Subsequent studies showed that methyl- and ethyl-dichlorophosphines[107,108], phenyldichlorophosphine[109], methyl phosphorodichloridite[110], and diethylaminodichlorophosphine[110] can enter into olefin oxidative chlorophosphination

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reactions. The reaction products in this case are mixed monochlorides of various acids based on pentavalent phosphorus.

III. REACTIONS OF THE CHLORIDES OF PHOSPHORUS(V) ACIDS WITH UNSATURATED COMPOUNDS

1. Reactions of the Chlorides of Phosphorus(V) Acids with Alkenes

A reaction of phosphorus pentachloride with unsaturated compounds was first described by Marsh and Gardner[111,112] in 1891–1894. They showed that camphene forms a complex compound with phosphorus pentachloride; its hydrolysis leads to camphenylphosphonic acid. In subsequent studies by Harnist[113], Bergman and Bondi[114-117], and other investigators[118-121] this reaction was extended to a large range of ethylenic and acetylenic hydrocarbons; the effect of their structure on the reactivity was established. These investigations were reviewed by Kabachnik[70] in 1947. In subsequent years new data accumulated, the range of application of this reaction was extended, and its mechanism was studied. Woodstock[122,123] and Kosolapoff[184] investigated the mode of addition of phosphorus pentachloride to asymmetric ethylenic hydrocarbons with a terminal double bond. Woodstock treated the complexes formed with phosphorus pentoxide or pentasulphide and obtained the dichlorides of chloroalkylphosphonic or chloroalkylphosphonothionic acids; he assumed that they had the structures $R-CH(POCl_2)CH_2Cl$ and $R-CH(PSCl_2)CH_2Cl$, and accordingly he postulated that the addition of phosphorus pentachloride to asymmetric ethylenes takes place contrary to the Markovnikov rule. Kosolapoff[121,124] showed that Woodstock's conclusions were erroneous. From the complex of phosphorus pentachloride with but-1-ene, he obtained the dichloride which he esterified and converted the product by dehydrochlorination into the ester of an unsaturated phosphonic acid. When this ester was ozonolysed, propionaldehyde was formed. Kosolapoff thus showed that the addition of phosphorus pentachloride to asymmetric olefins takes place in accordance with the Markovnikov rule:

$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHCl{-}CH_2PCl_4.PCl_5$$

$$\xrightarrow[\text{or } SO_2]{P_2O_5 \text{ or } P_2S_5} \begin{cases} RCH{=}CH{-}PCl_2 \\ \| \\ O \end{cases} \qquad \begin{cases} RCH{=}CH{-}PCl_2 \\ \| \\ S \end{cases}$$

Dibromo- and tribromo-isosafrole[125] and also vinyl and allyl chlorides[126] (at 20°C in benzene) react with phosphorus pentachloride to yield only chlorination products, chlorine adding to the double bond. At 100–110°C under pressure vinyl and allyl chlorides give, together with their double-bond chlorination products, also halogenohydrocarbons with twice as many carbon atoms as the initial olefin.

Kirsanov and coworkers[127,128] made interesting studies on the structure of the complexes formed. Before their investigation, it was assumed (without experimental justification) that the complexes formed from phosphorus pentachloride and olefins are β-chloroalkyltetrachlorophosphoranes $RCHCl-CH_2PCl_4$ or their double salts with phosphorus pentachloride[129-133]. The complexes were not isolated in a pure form. Fedorova and Kirsanov[127,128] were the first to suggest that the reaction of phosphorus pentachloride, which consists in the crystalline state of the tetrahedral cation $P^{(+)}Cl_4$ and the octahedral anion $P^{(-)}Cl_6$, with unsaturated compounds takes place by an ionic mechanism:

$$RCH{=}CH_2 + \overset{(+)}{P}Cl_4 \rightarrow (RCH{-}CH_2PCl_4)^{(+)} \rightarrow HCl + (R{-}CH{=}CH{-}PCl_3)^{(+)} \xrightarrow{\overset{(-)}{PCl_6}} RCH{=}CH{-}\overset{(+)}{P}Cl_3 \cdot \overset{(-)}{P}Cl_6.$$

With styrene as an example, it was shown that the complex formed is $C_6H_5CH{=}CH{-}P^{(+)}Cl_3P^{(-)}Cl_6$. At 70°C its yield was about 70%. The structure of this complex is confirmed by reactions with sulphur dioxide, styrene, and red phosphorus:

$$C_6H_5CH{=}\overset{(+)}{C}HPCl_3 \cdot \overset{(-)}{P}Cl_6{-} \begin{cases} \xrightarrow{2SO_2} POCl_3 + 2SOCl_2 + C_6H_5{-}CH{=}CH{-}P(O)Cl_2 \\ \xrightarrow{C_6H_5CH=CH_2} HCl + 2C_6H_5CH{=}CH{-}PCl_4 \xrightarrow{SO_2} \xrightarrow{P} \\ \xrightarrow{1\frac{1}{3}P} 2\tfrac{1}{3}\,PCl_3 + C_6H_5CH{=}CH{-}PCl_2 \end{cases}$$

Similar complexes were obtained in yields up to 70% when phosphorus pentachloride was allowed to react with the dichlorides of arylphosphonic acids:

$$ArPOCl_2 + 2PCl_5 \rightarrow POCl_3 + \overset{(+)}{ArP}Cl_3 \cdot \overset{(-)}{P}Cl_6.$$

On reduction with red phosphorus, they are converted into aryldichlorophosphines. It was shown, using the reaction of phenyltetrachlorophosphorane with styrene as an example[134], that hydrogen chloride formed in the reaction dissolves in phenylstyryltrichlorophosphorane and can be removed when the latter is reprecipitated from phosphorus oxychloride with petroleum ether or by vacuum distillation:

$$C_6H_5CH{=}CH_2 + C_6H_5\overset{(+)}{P}Cl_3 \rightarrow C_6H_5\overset{(+)}{C}HCH_2(C_6H_5)PCl_3 \xrightarrow{Cl^{(-)}}$$

$$\rightarrow HCl + C_6H_5CH{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}PCl_3 .$$

Phenylacetylene reacts with phenyltetrachlorophosphorane by a similar mechanism, but the α-carbon atom in the initially formed cation $C_6H_5\overset{(+)}{C}{=}CH{-}P(C_6H_5)Cl_3$ is more firmly bound to the hydrogen, as a result of which the chloride ion adds to the most electropositive β-carbon atom:

$$C_6H_5\overset{(+)}{C}{=}CHP(C_6H_5)Cl_3 \xrightarrow{Cl^{(-)}} C_6H_5CCl{=}CH{-}P(C_6H_5)Cl_3.$$

In the reaction of styryltetrachlorophosphorane with styrene and of β-chlorostyryltetrachlorophosphorane with phenylacetylene[135], distyryltrichlorophosphorane and di-(β-chlorostyryl)trichlorophosphorane were obtained respectively:

$$C_6H_5CH{=}CH{-}PCl_4 + C_6H_5CH{=}CH_2 \rightarrow (C_6H_5CH{=}CH)_2PCl_3 + HCl ,$$

$$C_6H_5CCl{=}CHPCl_4 + C_6H_5C{\equiv}CH \rightarrow (C_6H_5CCl{=}CH)_2PCl_3.$$

The structure of the complexes of phosphorus pentachloride with ethylenic hydrocarbons is consistent with the studies on their reduction. Walsh et al.[136] obtained alkenyldichlorophosphines by reducing complexes of olefins and phosphorus pentachloride with phosphorus in the presence of iodine:

$$3RCH{=}CHPCl_4 + 2P \xrightarrow{I_2} 3RCH{=}CHPCl_2 + 2PCl_3.$$

Kamai et al.[137] also obtained these compounds using antimony:

$$3(CH_3)_2C{=}CH_2 + 6PCl_5 \xrightarrow[-HCl]{} [(CH_3)_2C{=}\overset{(+)}{C}HPCl_3][PCl_6^{(-)}] \xrightarrow{4Sb}$$

$$\rightarrow 4SbCl_3 + 3PCl_3 + 3(CH_3)_2C{=}CHPCl_2.$$

Grechkin and Kalabina regard the reaction between phosphorus pentachloride and olefins as electrophilic substitution of hydrogen, adopting a mechanism[138] very similar to

that proposed by Fedorova and Kirsanov. The authors[138] suggest that a π-complex of the olefin and the cation $P^{(+)}Cl_4$ forms initially and is then converted into a stable complex with elimination of hydrogen chloride: $[RCH{=}CH{-}PCl_3]^+$. The latter reacts with a chloride ion and is converted into an alkenyltetrachlorophosphorane or reacts with the ion $P^{(-)}Cl_6$ to form a saltlike product. It can also form in the reaction between the alkenyltetrachlorophosphorane and phosphorus pentachloride:

$$RCH{=}CH_2 + \overset{(+)}{P}Cl_4 \rightarrow [RCH{-}CH_2PCl_4]^{(+)} \xrightarrow{-HCl} \cdot [RCH{=}CH{-}PCl_3]^{(+)} \xrightleftharpoons{Cl^{(-)}} RCH{=}CH{-}PCl_4$$

$$RCH{=}CH{-}PCl_4 \xrightarrow{PCl_5} \xrightarrow{RCH=CH_2} \xrightarrow{\overset{(-)}{P}Cl_6} [RCH{=}CHPCl_3]^{(+)}[PCl_6]^{(-)}.$$

The reaction between phosphorus pentachloride and acetylenic hydrocarbons has been less investigated. The reaction of phenylacetylene[117,129] with phosphorus pentachloride yields a complex, which, after treatment with sulphur dioxide, gives rise to the dichloride of β-chloro-β-phenylvinylphosphonic acid, while on hydrolysis it is converted into β-chloro-β-phenylvinylphosphonic acid itself:

$$C_6H_5C{\equiv}CH + 2PCl_5 \rightarrow C_6H_5CCl{=}CH{-}\overset{(+)}{P}Cl_3 \cdot \overset{(-)}{P}Cl_6 \xrightarrow{SO_2} C_6H_5CCl{=}CH{-}\overset{O}{\overset{\|}{P}}Cl_2$$

$$\xrightarrow{H_2O} C_6H_5CCl{=}CH{-}\overset{O}{\overset{\|}{P}}(OH)_2$$

p-Nitrophenylacetylene, diphenylacetylene, and phenylethylacetylene do not react with phosphorus pentachloride[117]. However, Bergman and Bondi[117] succeeded in obtaining 2-chloro-3-phenylpropenylphosphonic acid from 1-phenylpropyne and phosphorus pentachloride. They explained this synthesis by postulating that initially 1-phenylpropyne isomerises to 3-phenylpropyne. By analogy with phenylacetylene, it was assumed that the ionic complexes and products obtained from alkynes[105,117] (5-ethoxy- and 5-phenoxy-pent-1-ynes[139]) and phosphorus pentachloride are vinylphosphine derivatives:

$$RC{\equiv}CH + 2PCl_5 \rightarrow RCCl{=}CH\overset{(+)}{P}Cl_3 \cdot \overset{(-)}{P}Cl_6 \xrightarrow{SO_2} RCCl{=}CH{-}\overset{O}{\overset{\|}{P}}Cl_2 .$$

The position of the double bond was not determined. Meisters and Swan[140] observed in the NMR spectrum of the complex of oct-1-yne with phosphorus pentachloride an intense two-proton doublet (δ = 3.8 p.p.m., J = 17 Hz), indicating the presence of a CH_2 group bound to the phosphorus atom. They concluded that the ionic complexes and the substances obtained from them are allylphosphines and not vinylphosphine derivatives as was believed earlier. Not even traces of vinylphosphine derivatives were observed in any of the products even before their purification. The reaction with hexa-1,5-diyne involves only one acetylenic group. The authors assume that a rearrangement takes place after the electrophilic addition of $\overset{(+)}{P}Cl_4$ and then $\overset{(-)}{Cl}$ to the triple bond:

$$RCH_2C{\equiv}CH \xrightarrow{\overset{(+)}{P}Cl_4} \left[RCH_2{-}\overset{(+)}{C}{=}CHPCl_4\right] \xrightarrow{\overset{(-)}{Cl}} RCH_2{-}CCl{=}CHPCl_4 \rightleftarrows$$

$$\rightleftarrows \left[RCH{=}CCl{=}CHPCl_4\right]^{(-)} + H^{(+)} \rightleftarrows RCH{=}CCl{-}CH_2{-}PCl_4 .$$

Alternatively they assume that a rearrangement may occur in the carbonium ion with formation of an intermediate allene derivative. The migration of the chlorine atom from the phosphorus to the positively charged carbon can then complete the reaction:

$$RCH_2C{\equiv}CH \xrightarrow{\overset{(+)}{P}Cl_4} [RCH_2{-}\overset{(+)}{C}{=}CHPCl_4] \rightleftarrows RCH{=}C{=}CHPCl_4 + H^{(+)} \rightleftarrows$$

$$\rightleftarrows [RCH{=}\overset{(+)}{C}{-}CH_2PCl_4] \rightarrow RCH{=}CCl{-}\overset{(+)}{C}H_2PCl_3.$$

The new hypothesis which has been developed concerning the mechanism of the reactions of phosphorus pentachloride with unsaturated compounds permit certain conclusions about the reactivity of unsaturated hydrocarbons in these reactions. With increase of acidity in a series of unsaturated hydrocarbons, their phosphorylation with phosphorus pentachloride should be facilitated, and this is indeed observed.

2. Reactions of Phosphorus Pentachloride with Hydrocarbons Containing a Conjugated System of Double and Triple Bonds

The first information about the reaction of phosphorus pentachloride with the simplest hydrocarbon containing a conjugated system of double bonds (divinyl) was published by Kosolapoff[141] in 1946. The complex formed in the reaction was treated with alcohol and the resulting chlorobutenylphosphonic esters were dehydrochlorinated to butadienylphosphonic esters. According to Kosolapoff's data, a mixture of diethylbuta-dien-1-yl- and diethylbutadien-2-yl-phosphonates was obtained. On this basis, it was suggested that the initial addition of phosphorus pentachloride took place in positions 1, 2 and 1, 4. In the subsequent studies by Short[142,143] and also by Anisimov and Kolobova[144-146] it was asserted that the addition of phosphorus pentachloride to divinyl takes place in position 1, 2. It has been shown[147] that these data are erroneous. It has been demonstrated by infrared spectroscopy and by syntheses that the decomposition of the complex of phosphorus pentachloride and divinyl with sulphur dioxide yields the dichloride of 4-chlorobut-2-enylphosphonic acid:

$$2PCl_5 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_2Cl{-}CH{=}CH{-}CH_2PCl_4 \cdot PCl_5 \xrightarrow{2SO_2}$$

$$\rightarrow CH_2Cl{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}H_2PCl_2 + POCl_3 + 2SOCl_2 .$$

The dialkyl esters of 4-chlorobut-2-enylphosphonic acid proved to be identical to those obtained in the reaction of 1,4-dichlorobut-2-ene with trialkyl phosphites:

$$ClCH_2{-}CH{=}CH{-}CH_2Cl + P(OC_2H_5)_3 \rightarrow ClCH_2{-}CH{=}CH{-}CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2.$$

$$ClCH_2{-}CH{=}CH{-}CH_2PCl_2 + 2C_2H_5OH \rightarrow ClCH_2{-}CH{=}CH{-}CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2.$$

Their oxidation with potassium permanganate gave chloroacetic acid. The 1,2-addition products could be present in the reaction mixture only as an impurity. The decomposition of the complex with hydrogen sulphide leads to the chloride of 4-chlorobut-2-enyl phosphonothionic acid. Butadienylphosphonic esters are very reactive compounds, which readily combine with nucleophilic reagents, enter into the diene synthesis reaction, and are capable of polymerisation and copolymerisation[148]. Isoprene[146,147] and 4-methylpenta-1,3-diene[148,149] react with phosphorus pentachloride to form 1,2-addition products. In the reaction of phosphorus pentachloride with phenylbutadiene in proportions of 1 : 3 and of phenyl- and styryl-tetrachlorophosphoranes with phenylbutadiene in proportions of 1 : 1, diphenylbutadienyltrichlorophosphorane, phenylbutadienyltrichlorophosphorane, and styrylbutadienyltrichlorophosphorane

are formed[150]. Vinylacetylene[151] and other hydrocarbons of this series, vinylethylacetylene[152], isopropenylacetylene[151,153], and ethynylcyclohexene[154], react with phosphorus pentachloride under mild conditions. The intermediate complexes were not isolated. They were immediately decomposed with sulphur dioxide. The dichloride of β-vinyl-β-chlorovinylphosphonic acid was obtained from vinylacetylene, the dichloride of β-cyclohexenyl-β-chlorovinylphosphonic acid was obtained from ethynylcyclohexene, and the dichloride of β-vinyl-β-chloro-α-ethylvinylphosphonic acid was obtained from vinylethylacetylene. It follows from these results that phosphorus pentachloride reacts with hydrocarbons of the vinylacetylene series to form products resulting from addition to the triple bond. Interesting results were obtained with isopropenylacetylene[153]. The final reaction product was the dichloride of 2-chloro-3-chloromethylbutadienylphosphonic acid together with 1,2,3,4-tetrachloro-3-methylbut-1-ene.

3. Reactions of the Chlorides of Phosphorus(V) Acids with Vinyl Ethers

This reaction, first described by Anisimov and Nesmeyanov[155], has attracted the attention of a large number of investigators in recent years. In a series of investigations Anisimov and Nesmeyanov showed that the reaction of phosphorus pentachloride with vinyl ethers yields complex compounds. The decomposition of these complexes with sulphur dioxide or with acetic acid results in the formation of the dichlorides of β-alkoxyvinylphosphonic acids[155-158].

$$RO{-}CH{=}CH_2 + 2\,PCl_5 \rightarrow RO{-}CHCl{-}CH_2PCl_4 \cdot PCl_5$$

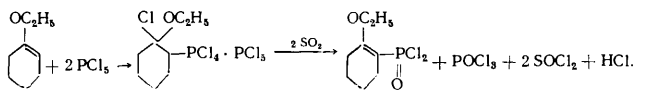
$$\xrightarrow{2\,CH_3COOH} ROCH{=}CHPCl_2 + POCl_3 + 2\,CH_3CCl + 3\,HCl$$

$$\xrightarrow{2\,SO_2} ROCH{=}CHPCl_2 + HCl + POCl_3 + 2\,SOCl_2.$$

A wide variety of alkyl vinyl ethers[144,155,156,158], monoalkyl vinyl ethers of ethylene glycol[157], and aryl vinyl ethers[144,159] were used in these reactions. β-Chloroethyl vinyl[160] and alkyl β-bromovinyl[161], ethers and vinyl sulphides[162] react similarly with phosphorus pentachloride. When the complexes are decomposed with hydrogen sulphide, the dichlorides of β-alkoxyvinylphosphonothionic acids are formed:

$$ROCHCl{-}CH_2PCl_4 \cdot PCl_5 + 2\,H_2S \rightarrow RO{-}CH{=}CH{-}\overset{S}{\overset{\|}{P}}Cl_2 + PSCl_3 + 5\,HCl.$$

Alkoxyvinylphosphonic and alkoxyvinylphosphonothionic esters, compounds which are very difficult to obtain by other methods, can be prepared in good yields by the esterification with alcohols of the dichlorides of β-alkoxyvinylphosphonic and β-alkoxyvinylphosphonothionic acids. When the ratio of the alkyl vinyl ethers to phosphorus pentachloride is 4 : 1, the chlorides of bis(β-alkoxyvinyl)phosphinic acid are obtained ultimately[163]. Arbuzov and coworkers carried out the reaction with phosphorus pentachloride of α-substituted vinyl ethers[164] and cyclic vinyl ethers with a double bond in the ring[165,166]. In these cases too the reactions take place in accordance with the general mechanism:



Apart from the decomposition of the complexes by various reagents, their reduction[167,168] and thermal decomposition[160] were investigated. When the complexes were treated with white phosphorus in the presence of iodine, β-alkoxyvinyldichlorophosphines were obtained, and the products of thermal decomposition were alkoxy-αβ-dichloroethyl vinyl ethers.

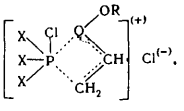
A number of studies have been made on phenyl- and alkyl-tetrachlorophosphoranes. Anisimov and Kolobova[169] studied the reaction of phenyltetrachlorophosphorane with ethyl vinyl ether. When the complex was treated with sulphur dioxide, the chloride of β-ethoxyvinylphenylphosphinic acid was formed, while treatment with white phosphorus in the presence of iodine gave β-ethoxyvinylphenylchlorophosphine. Similar results were obtained by Tsivunin et al.[170]. Thermal decomposition of the complex of phenyltetrachlorophosphine with n-butyl vinyl ether gives the chloride of β-chlorovinylphenylphosphinic acid[171]. In the thermal decomposition of the complex of ethyltetrachlorophosphorane with vinyl ethers[170,172], the same substance, the chloride of β-chlorovinylethylphosphinic acid, is formed regardless of the structure of the alkoxy-group:

$$CH_2{=}CH{-}OR + C_2H_5PCl_4 \xrightarrow{\Delta} C_2H_5\overset{O}{\overset{\|}{P}}(Cl){-}CH{=}CHCl + RCl + HCl.$$

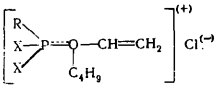
The reactions with diethyl and diphenyl-trichlorophosphoranes take place in an interesting way. Diethyltrichlorophosphorane forms with n-butyl vinyl ether a complex which has the structure of diethyl-α-chloroethoxydichlorophosphorane[173]:

$$(C_2H_5)_2PCl_3 + CH_2{=}CH{-}OC_4H_9 \rightarrow (C_2H_5)_2\overset{Cl}{\overset{|}{P}}(Cl){-}O{-}\overset{Cl}{\overset{|}{C}}H{-}CH_3 + (C_4H_9)_n.$$

Thermal decomposition of this complex leads to the chloride of diethylphosphinic acid. In the reactions of diphenyltrichlorophosphorane and triphenyldichlorophosphorane with n-butyl vinyl ether, diphenyl-α-chloroethoxydichlorophosphorane and triphenyl-α-chloroethoxychlorophosphorane were obtained respectively. It is suggested[173] that in these reactions the vinyl ether molecule forms with the phosphorus chloride a many-centre system due to the presence of the free *d*-orbitals of phosphorus and the conjugated system of $p\pi$-electrons (π-complex):



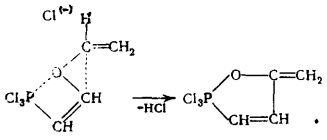
Compared with phosphorus pentachloride, the population of the $d\pi$-orbitals of phosphorus and chlorides of the type $RPCl_4$, R_2PCl_3, and R_3PCl_2 gradually decreases. This leads to an increase in the stability of the π-complexes:



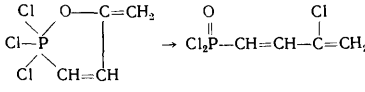
where X may be R or Cl. Their thermal decomposition leads to the formation of a large amount of the chlorides of alkylphosphonic or dialkylphosphinic acids.

The σ-stabilisation of the complexes is due to the formation of β-alkoxyvinylalkylchlorophosphoranes. These postulates were also used to account for the mechanism of the reaction of phosphorus pentachloride with divinyl ether[174,175]. The decomposition of the complex with hydrogen sulphide

leads to a crystalline product, the formation of which can be represented by the mechanism



When the product is heated, the dichloride of γ-chlorobutadienylphosphonic acid is formed:

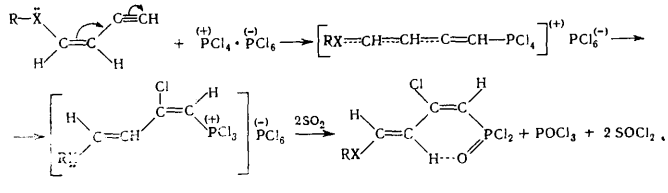


The structure of the cyclic product is consistent with PMR and NMR spectra.

Shostakovskii and coworkers[176-178], who investigated the reactions of phosphorus pentachloride with alkyl ethynylvinyl ethers and alkyl ethynylvinylsulphides, initially suggested that they take place at the double bond with formation (after decomposition of the complexes with sulphur dioxide) of products with the structure

$$ROCH{=}C(POCl_2){-}CCl{=}CH_2 \text{ and } RSCH{=}C(POCl_2){-}CCl{=}CH_2.$$

Subsequently they showed that their initial hypotheses were erroneous[179]; the reaction takes place at the triple bond in accordance with the mechanism:



where X = O or S. The products are the dichlorides of 4-alkoxy(alkylthio)-2-chlorobuta-1,3-dienylphosphonic acids.

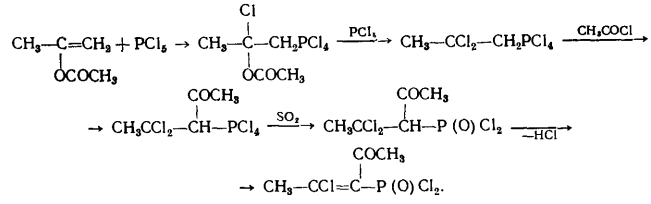
A very convenient method for the synthesis of the dichlorides of alkoxyvinylphosphonic acids or β-alkoxy-α-alkylvinylphosphonic acids has been recently developed by Petrov et al.[180] It is suggested that phosphorus pentachloride be allowed to react with ethers, which, after chlorination, are dehydrochlorinated and converted into vinyl ethers:

$$ROCH_2{-}CH_2R' + PCl_5 \xrightarrow{-HCl} ROCHCl{-}CH_2R' \xrightarrow{-HCl} RO{-}CH{=}CHR'.$$

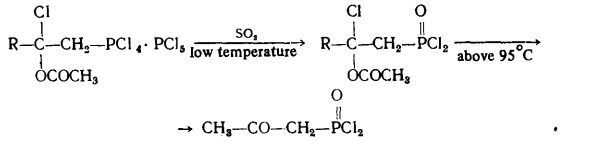
Subsequently the reaction takes place by the usual mechanism. When the complex is treated with hydrogen sulphide, the dichlorides of β-alkoxy-α-alkylvinylphosphonothionic acids are formed in yields up to 80%. This simple reaction makes it possible to obtain a number of interesting organophosphorus compounds.

4. Reactions of Phosphorus Pentachloride with Enol Esters

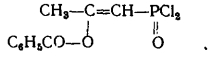
Lutsenko and Kirilov, who were the first to investigate reactions of this type, suggested that in the first stage the usual mechanism obtains; the addition product formed is then chlorinated by phosphorus pentachloride this being followed by reaction with acetyl chloride[181]: Treatment of the complexes with sulphur dioxide should yield the dichlorides of α-acetyl-ββ-dichloroalkylphosphonic acids:



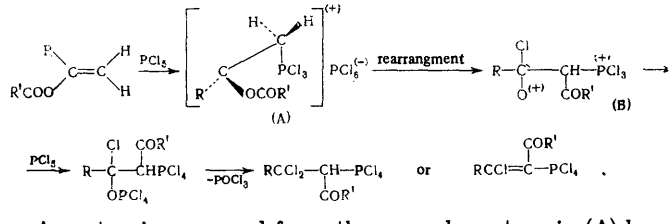
The authors isolated the initial complex at a low temperature. Its treatment with sulphur dioxide yields the dichlorides of β-acetoxy-β-chloroalkylphosphonic acids[182-184]. On heating, acetyl chloride is given off and the complex is converted into the dichloride of acetonylphosphonic acid:



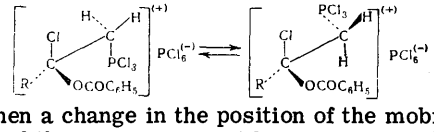
With the benzoate ester, evolution of hydrogen chloride from the complex and the ultimate formation of an unsaturated acid chloride were observed[185]:



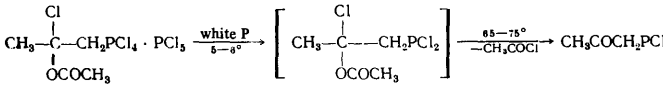
Subsequently, in order to explain the mechanism of the reaction of phosphorus pentachloride with enol esters, the authors suggested a new mechanism involving the intramolecular rearrangement of the complex formed initially[185-187]:



A proton is removed from the α-carbon atom in (A) by the anion $PCl_6^{(-)}$. The resulting dipolar ion (B) reacts with phosphorus pentachloride and is converted into the intermediate (C), which then breaks down the formation of the final products. When account is taken of the conformation of the intermediate complex (A), this mechanism can explain, for example , the unusual behaviour of isopropenyl benzoate in the reaction with phosphorus pentachloride. Because of the large size of the benzoyloxy- and PCl_3 groups, their *cis*-disposition in the complex is difficult; the conformation involving the *trans*-disposition of the groups is more favourable:



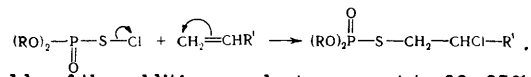
There is then a change in the position of the mobile hydrogen atom and the rearrangement becomes more difficult—the *trans*-elimination of hydrogen chloride becomes more probable. When the complexes (A) are reduced with white phosphorus at a low temperature (5-6°C), i.e. under conditions excluding the possibility of rearrangement, β-oxoalkyldichlorophosphine is formed[167]:



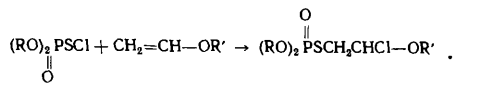
At a higher temperature (10–12°C), the reaction takes place in two ways–reduction and rearrangement. The products are then acetonyldichlorophosphine and the dichloride of α-acetyl-β-chloropropenylphosphonic acid.

5. Addition of Dialkoxyphosphinothiolic and Dialkoxyphosphinoselenolic Chlorides to Unsaturated Compounds

Dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides contain a very mobile halogen atom which ensures the ready addition of these compounds to a multiple carbon–carbon bond. Dialkoxyphosphinothiolic chlorides have been obtained by the action of chlorine or sulphuryl chloride on dialkyl phosphorothioates, trialkyl phosphorothionates, and bis(dialkoxyphosphinyl) disulphides. Diethoxyphosphinoselenolic chloride was obtained by the action of sulphuryl chloride on triethyl phosphoroselenoate[188]. Michalski and coworkers, who were the first to obtain compounds of this type, achieved their addition to a number of symmetrical and asymmetric hydrocarbons of the ethylene series: ethylene[189–192], propene[193], isobutene[194], tetramethylethylene[189], cyclohexene[188], styrene, and stilbene[195]. The reactions take place very readily when the gaseous hydrocarbons are passed through and liquid hydrocarbons are slowly added to the dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides at room or a lower temperature, usually in benzene solution. With asymmetric olefins, the mode of addition of the reagents is determined by their polarisation:



The yields of the addition products amount to 60–95%. Dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides also add very readily to vinyl ethers[188,196,197] and vinyl sulphides[198]. In these reactions too the mode of addition is determined by the nucleophilic properties of the double bond with electron-donor alkoxy- or alkylthio-substituents:



Of the compounds with a conjugated system of double bonds, only divinyl has been used in the reaction with diethoxyphosphinothiolic chloride[199]. The 1,2-addition product is formed:

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The Concept of Electronegativity. Conclusions and Prospects†

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The principal methods for the determination of the electronegativity (EO) of the elements and radicals are examined—thermochemical, structural, spectroscopic, quantum-chemical, and a method based on ionisation potential. Particular attention is drawn to the necessity of taking into account the characteristic features of the chemical bond—its multiplicity and degree of hybridisation. The problems of the dimensions of the electronegativity of the elements are discussed. A compilation of the recommended electronegativities of atoms, radicals, and ions is given.
The principal applications of the concept of electronegativity are discussed: the determination of the atomic charges in molecules and crystals (good agreement between experimental and theoretical values is demonstrated); an estimate of the multiplicity of chemical bonds in inorganic ions and compounds, which agrees with the determination from the geometrical or spectroscopic characteristics of these substances; the principal physicochemical properties and the behaviour of inorganic substances as a function of the ionic character of their bonds and the difference between the electronegativities of the constituent atoms have been examined (semiconductor and molecular-physical characteristics, acid-base relations, specific features of the trans-effect of atoms in the inner sphere of platinum compounds, the possibility of the synthesis of new inorganic substances). The controversial questions of the nature and limits of applicability of the concept of electronegativity in general chemistry are briefly discussed.

CONTENTS

I. Introduction 332
II. Methods for the determination of electronegativity 333
III. The scope of the application of the concept of electronegativity 338

I. INTRODUCTION

More than one hundred years ago Berzelius[1] put forward the brilliant hypothesis concerning the electrical nature of chemical forces and divided all atoms into electropositive and electronegative. Lewis's theory gave rise to a concrete concept of polarity—regarded as the result of the displacement of the centre of gravity of the electron cloud of the bond towards one of the atoms, which is in fact electronegative in the given molecule.

More intensive experimental studies on polar molecules by various physical methods created the conditions for a new important scientific theory, whose author was Pauling[3]. The latter introduced into chemistry the concept of electronegativity (EO) defined as the capacity of the atom in a molecule (or in general in a compound) to attract valence electrons, and indicated an experimental method for its quantitative determination. This study gave rise to many other attempts to determine empirically the electronegativities of elements with the aid of geometrical, spectroscopic, and energy characteristics of atoms in molecules.

However, towards the beginning of the 1950's it became clear that the electronegativity of the element is not in most cases a constant property of the latter, but depends on the valence and degree of hybridisation of the bonds. Therefore special experimental and quantum-chemical investigations were begun in order to determine the electronegativity of atoms in various valence states and to find the electronegativities of whole groups of atoms (radicals).

The history of the development of the concept of electronegativity (up till 1961) is described in the present author's monograph[4] and the present review therefore considers mainly recent studies, which have made the greatest contributions to the theory and practical application of electronegativity in chemistry. Here too the principal conclusions following from the controversy on the meaning and limits of applicability of the concepts of electronegativity, which took place in recent years in the Soviet Union and to some extent abroad, will be described.

† In publishing this article, the Editorial Board consider it necessary to inform the readers that, although they do not agree with some of the author's views, the publication of the review is useful, since it will enable a wide circle of chemists to become familiar with the present state of the problem.

II. METHODS FOR THE DETERMINATION OF ELECTRONEGATIVITY

Any empirical method for the determination of electronegativity can be used also for the solution of the converse problem, i.e. the calculation of the corresponding physicochemical characteristic of the substance. Therefore particular attention is given here to quantitative methods for the determination and interpretation of electronegativity.

1. The Use of Thermochemical Data

Pauling[3] represented the difference between the energies of the real and purely covalent bonds between atoms A and B in the form of two terms—the electronegativities of the two species involved in the bond:

$$X_A - X_B = 0.208\{E(A-B) - {}^1/_2[E(A-A) + E(B-B)]\}^{1/2}, \quad (1)$$

where X denotes the electronegativity. Bearing in mind that the expression in braces in Eqn. (1) is equal to the heat of reaction Q, Eqn. (1) may be written in the more compact form

$$\Delta X_{AB} = 0.208Q\,. \quad (2)$$

Both these equations assume an arithmetical mean method for the calculation of covalent bond energies. In view of the correlation between bond strength and the product of the atomic wave functions, Pauling suggested that geometric means be used for the calculation of covalent bond energies, i.e. he replaced $\frac{1}{2}[E(A-A) + E(B-B)]$ by $[E(A-A) \times E(B-B)]^{1/2}$. Apart from being theoretically correct, such replacement made it possible to eliminate the disadvantage that in a number of cases (for example in alkali metal hydrides) the energy difference between $E(A-B)$ and half the sum of $E(A-A)$ and $E(B-B)$ were less than zero. By postulating that the electronegativity of hydrogen is 2.1, Pauling was able to calculate the absolute electronegativity of a large number of elements in the Periodic System. The most accurate and most complete data on the "thermochemical" electronegativities are given by Allred[5].

Comparison of Allred's system with Pauling's initial table reveals in a number of cases deviations in the electronegativities exceeding the effect of the experimental error in the determination of the bond energies. They are due to the use in the calculations of a large number of new thermochemical data for various bonds of the same element. If this entails not only a change in the polarity but also in the degree of hybridisation of the bonds, Eqn. (1) automatically reflects all the effects as changes in electronegativity.

At the present time there are unfortunately no general methods for an *a priori* determination of the type and degree of hybridisation, except for the thoroughly investigated case of carbon. Nevertheless the importance of this factor in the calculation of electronegativity is obvious and was recently again demonstrated by Dobrotin[6,7] for rare-earth compounds. Therefore, in relation to the concept of electronegativity, the problem is solved by a purely empirical procedure, by determining the electronegativities of whole groups of atoms (radicals) thereby taking into account the immediate environment of the given atom. This method was first used in 1955 by Pritchard and Skinner[8] and then by Finemann[9,10].

The latter author suggested that the thermochemical electronegativities of radicals be calculated from Pauling's Equation (1), with the atom B replaced by the radical R. It is then necessary to bear in mind that the energy of one of the covalent bonds must also be included in the calculation in the form $E(R-R)$. In some studies this was disregarded and incorrect values were obtained as a result.

The electronegativities of polyvalent atoms or free radicals, for example of the type AB, where A is a di- or tri-valent metal and B a halogen, can be calculated by the thermochemical method. Such calculations were recently performed by the present author[11] with the aid of the formula

$$\Delta X^s_{A^\bullet-B} = \Delta X^s_{A-B} + 0.433[(E_{A^\bullet-B} - E_{A-B}) + {}^1/_2(E_{A-A} - E_{A^\bullet-A^\bullet})]\,, \quad (3)$$

which can be readily derived from Pauling's basic equation for a normal molecule and a free radical. The results of the calculations are presented in Table 1, which includes for comparison the electronegativities of metals in the covalent state used in the calculation. Table 1 shows that the difference between the electronegativities of the metals decreases on formation of free radicals. The physical reason for this consists in the effect of free electrons on bond energies. Thus the presence of a free electron pair lowers the electronegativity of the atom in consequence of the repulsion between this pair and the valence electrons (in Group III elements); an isolated electron has a dual effect —on the one hand it repels the valence electrons and therefore lowers the electronegativity and on the other hand it increases the contribution to bond energy due to electron pairing. Evidently the repulsion effect of the free electron will predominate in small atoms (beryllium) and will gradually decrease with increasing interatomic distances (magnesium etc.); the spin–spin interaction does not depend on bond length and therefore begins to predominate in large atoms (calcium, strontium, and barium).

Table 1. Electronegativities of metals in free radicals.

Atom	$X_{A^\bullet}$	X_A	Atom	$X_{A^\bullet}$	X_A
Be	1.3	1.5	B	1.6	2.0
Mg	1.2	1.2	Al	1.3	1.5
Ca	1.2	1.0	Ga	1.2	1.6
Sr	1.2	1.0	In	1.2	1.7
Ba	1.2	0.9			
Zn	1.5	1.6			
Cd	1.5	1.7			

In concluding the description of the results derived by classical thermochemical methods for the determination of electronegativities, data will be presented on the effect of bond multiplicity using the carbon atom as an example. Approximate calculations showed[4] that the electronegativity of carbon decreases in the direction of the multiple bond ($X_{C=} = 2.1$, $X_{C\equiv} = 2.0$), increasing in the opposite direction ($X_{=C-} = 2.9$, $X_{\equiv C-} = 3.6$). Calculation of the average electronegativity of the carbon atom yields $X = 2.5$ for ethylenic carbon and $X = 2.4$ for acetylenic carbon. Thus, on formation of a multiple bond, the capacity of the atom to attract valence electrons changes.

The thermochemical method is the first and fairly accurate procedure for the determination of the electronegativities of the elements and is therefore frequently used as a comparison scale for other methods of calculation of atomic electronegativity. However, it should be recalled that it is not free from disadvantages. Apart from the considerations described above, one other factor

must be pointed out. In Pauling's equation it is postulated that the energy of a polar bond consists of the constant energy of the covalent bond and an additional "ionic" energy, although it is evident that, with increasing ionisation of the atom, the coulombic component of the bond energy will increase and the covalent component will fall. Energetic methods for estimating atomic charges, which will be examined below, have been developed on this basis.

Although the basic equation is formally incorrect, in practice the energy of the covalent bond varies within a small range, as can be readily shown by calculating, for example, the overlap integrals for purely covalent and purely ionic bonds of the same atoms at fixed distances. Furthermore the energy of the covalent bond is significantly lower than the electrostatic energy of the interaction between the same atoms over the same distance and therefore even a large relative error in the covalent components of the energy introduces a small absolute error into the final result.

Recently McDaniel and Yingst[12] proposed a new thermochemical procedure for the calculation of the electronegativities of atoms and radicals. By considering the thermochemical cycle for the dissociation of an acid and its oxidation in aqueous solution, the authors arrived at the following expression after a number of simplifications (and reasonable assumptions):

$$0.059\,\mathrm{pK}\,\Omega - E^0 = (X_A - X_H)^2\,, \qquad (4)$$

where E^0 is the electromotive force of the half-cell in the oxidation of the acid residue A^- and $pK\Omega$ was determined for the acid HA at 25°C. It is significant that it proved possible to calculate by means of this equation the electronegativities not only of elements but also of a number of molecular radicals.

The "thermochemical" electronegativities will be used by the present author subsequently in the compilation of a table of electronegativities.

2. The Use of Geometrical Characteristics

The electronegativity of an atom is evidently determined by the force of attraction of its valence electrons by the effective charge of the nucleus. Therefore it is quite reasonable to employ the geometrical characteristics of atoms and molecules for the calculation of electronegativity.

The concept of electronegativity was first applied in the calculation of interatomic distances by Schomaker and Stevenson[13], who suggested that the bond length be calculated from the formula

$$r_{AB} = r_A + r_B - 0.09\Delta X_{AB}\,, \qquad (5)$$

where r_A and r_B are covalent radii. The Schomaker–Stevenson formula was subsequently justified quantum-chemically and found numerous applications[14–18]; it led to the possibility of the solution of the converse problem—the calculation of electronegativities from atomic radii. The general form of the corresponding equations is

$$X = a\frac{Z^*}{r^n} + b\,, \qquad (6)$$

where $n = 1$ in Gordy's formula[19] and $n = 2$ in Allred and Rochow's equation[20]. The principal result of the application of these expressions is that, for atoms having the inert gas electronic structure, the "geometrical" electronegativities are close to the thermochemical values, but, for atoms containing d- and f-electrons in the outer or penultimate shell, the "geometrical" electronegativities are significantly smaller than the generally accepted values. For example, the thermochemical electronegativities for the copper and zinc subgroups are[5]:

Cu	Ag	Au	Zn	Cd	Hg
1.90	1.93	2.54	1.65	1.69	2.00 .

while the values obtained by Gordy and by Allred and Rochow are respectively:

0.96	0.91	0.92	1.21	1.13	1.12
1.75	1.42	—	1.66	1.46	—

The reason for this difference lies in the inadequacy of Slater's rules, which were used to calculate the effective nuclear charge. The more accurate system of Z^* values put forward recently[21] made it possible to bring the geometrical and thermochemical electronegativities much closer together, the difference between the two series of values remaining virtually the same throughout the Periodic System. For example, the average geometrical electronegativities for metals in copper and zinc subgroups are[22]:

Cu	Ag	Au	Zn	Cd	Hg
1.74	1.66	1.97	1.76	1.68	1.80 .

A disadvantage of the geometrical method for the calculation of electronegativities in some cases is the indeterminate valence state of the element in a number of simple compounds from which the interatomic distances were taken. However, in most cases there is no doubt about the valence of the atoms for which the geometrical electronegativity is calculated, and therefore the latter may be used in the compilation of the electronegativities of the elements.

Using the geometrical method, it is possible to determine the electronegativities of carbon atoms involved in multiple bonds. These calculations were performed between 1960 and 1964 [4,22,23] and their results are in good agreement with the data derived by the thermochemical method. When account is taken of the fact that the effective nuclear charge of the carbon atom also depends somewhat on the state of hybridisation and when appropriate ionisation potentials are used to calculate Z^*, then, on the basis of $Z^* = 3.25$ adopted for sp^3-hybridisation, it is easy to show that in the direction of the multiple bond $Z^*_C = 3.09$, $Z^* = 3.39$, for sp^2-hybridisation, and $Z^* = 3.64$ for sp-hybridisation. Hence, using the Allred–Rochow equation and the Gordy–Batsanov formula and also the geometrical characteristics of the multiple bonds taken from the literature[4,22], we arrive at the following electronegativities: 2.5 for sp^3-hybridisation, 2.7 for sp^2-hybridisation, 3.1 for sp-hybridisation, 2.2 for the double bond, and 2.1 for the triple bond.

Thus, if on formation of a multiple bond the electronegativity of the atom decreases in the direction of the bond, the effective charge of the atomic nucleus and its electronegativity become saturated as a result of the enhanced attraction of electrons from the opposite side of the atom. The geometrical method has also been applied in the calculation of the electronegativities of radicals. The first attempt was made by Wilmshurst[24], but, although the results were acceptable in practice, they were nevertheless incorrect from a formal standpoint[4]. A more successful attempt was made by Yan[25], who calculated the electronegativities of radicals with the aid of the equation

$$X = a\frac{n^*}{r^*} + b\,, \qquad (7)$$

where r^* is the effective radius of the central atom of the radical and n^* the number of effective valence electrons

(i.e. actually Z^*) calculated by Sanderson's method (see below).

Somewhat isolated from the trend discussed here is a whole series of studies by Sanderson[26-28], who observed that the average electron density of atoms varies in parallel with their electronegativity. By expressing the electron density of the element as a fraction of the electron density of the corresponding inert gas, Sanderson obtained quantities which he called "stability ratios" (SR) and which are tabulated in the present author's monograph[4] and will not be quoted here. The stability ratios and Pauling's electronegativities are simply related:

$$X^{\frac{1}{2}} = 0.21 \quad \mathrm{SR} + 0.77 \ . \tag{8}$$

We shall return to these studies later.

3. The Use of Spectroscopic Data

The first paper describing the relation between electronegativity and spectroscopic characteristics was published by Gordy[29], who established the following empirical relation:

$$k_{AB} = aN \left(\frac{X_A X_B}{r^2}\right)^{0.75} + b \ , \tag{9}$$

where r is the atomic distance, N the bond multiplicity, a and b are constants, and k is the force constant of the bond. Gordy's "spectroscopic" electronegativities are in good agreement with the thermochemical and geometrical values. However, the use in calculations of electronegativity of dynamic proportionality coefficients reduces the value of Gordy's method, because the determination of bond force constants frequently constitutes a difficult independent problem. Therefore subsequent development of the spectroscopic determination of the electronegativities of atoms and radicals involved the establishment of a direct relation between electronegativities and characteristic vibration frequencies. Without dwelling on the history of the problem, only the general form of functions used will be indicated[30-33]:

$$\nu = a + bX \ . \tag{10}$$

Such a linear relation is at first sight incomprehensible, but if the force constant of a polar bond is put in the simplest form:

$$k \simeq c \frac{Z_1^* Z_2^*}{r^3} \tag{11}$$

and the formula for a harmonic oscillator is then used, it is readily seen that

$$\nu \propto \frac{Z^*}{r^{1.5}} \ . \tag{12}$$

Comparison of Eqns. (6) and (12) shows that the exponent of the atomic radius in Eqn. (12) is the average of the values of n from Gordy's and Allred and Rochow's formulae, i.e. Eqn. (12) is essentially identical with Eqn. (10). Since the latter equation does not involve the mass of the vibrating atoms, in the calculation of electronegativities one usually compares the frequencies of the same A–B bond in molecules of the type ABC_n, where C_n is a variable atom or radical. However, comparison of the data of various workers shows that there is a considerable scatter in their results, which can be explained by the fact that bond frequencies cannot strictly be regarded as isolated, being influenced by the geometry of the molecule in addition to the nature of the chemical bond.

Like the thermochemical and the geometrical procedures, the spectroscopic method shows that the electronegativity of the atom increases in the direction opposite to that of the multiple bond and to a greater extent the larger is the multiplicity of the bond. In the direction of the multiple bond itself, the atomic electronegativity of carbon falls, as follows from the application of Gordy's formula to this case[23]: if it is assumed that $X_C = 2.5$, we have 2.3 and 2.2 respectively for C= and C≡ and similarly for nitrogen we have $X_{N=} = 3.0$ and $X_{N\equiv} = 2.8$.

The calculation of electronegativities from electronic spectroscopic data (optical electronegativities) is very interesting. Here mass does not play a significant role and therefore it is possible in principle to obtain more accurate values. Jörgensen and coworkers[34-36] showed that the wave number of the electronic transition for complexes of the type $MHal_n$ is proportional to the difference between the electronegativities of the central atom and the halogen. On the basis of the generally accepted electronegativities of the halogens, the authors obtained a number of electronegativity values for complex-forming metals.

This development in the calculation of atomic electronegativities is very promising; calculations of this kind can probably detect effects such as the trans-effect and other forms of interatomic interaction in the inner sphere of complex compounds.

Apart from the relation between electronegativities and vibration spectra, definite relations between the electronegativities of atoms and radicals on the one hand and spectroscopic characteristics on the other have been observed also in the radiowave part of the spectrum. This field was pioneered by Dailey and Shoolery[37], who established that the chemical shift (CS) of the nuclear magnetic resonance frequency of the hydrogen atom in alkyl derivatives is linearly related to the electronegativities of the radicals linked to the carbon atom:

$$X = 0.01158\delta + 1.71 \ , \tag{13}$$

where δ is the internal chemical shift in the ethyl group between α- and β-protons. Since these measurements were made in benzene solution and the latter exhibits an anomalous dilution effect, Cavanaugh and Dailey[38] later repeated the measurements in carbon tetrachloride solution and obtained more reliable data, which are described by the equation

$$X = 0.0114\delta + 1.78 \ . \tag{14}$$

The electronegativities of oxygen-containing radicals[39], Group IV elements[40], and Group IIb metals[41] have been calculated from similar equations.

Comparison of "radiowave" electronegativities with the "optical" values shows that in most cases the agreement is satisfactory. However, the electronegativities of certain radicals and in particular of CN, are significantly smaller than the generally accepted values. The reason for this lies in the inadequacy of the method of calculation of electronegativity from an equation of the type of Eqn. (14). Heel and Zeil[42,43] showed that, to a first approximation, the chemical shift measured experimentally consists additively of a term which depends on the chemical bond and terms characterising the geometry of the molecule only:

$$\delta = a + b + c + d \ , \tag{15}$$

where a is determined by the chemical difference between the protons, b is a diamagnetic correction which depends on the trial form adopted, c depends on the intermolecular interaction, and d characterises the magnetic anisotropy of the atoms and radicals within the molecule. The low value

of the "radiowave" electronegativity is due to the neglect of the factor d by Dailey and Shoolery[37].

To avoid errors, Heel and Zeil suggest that the comparative method be used to establish the relation between the chemical shift and electronegativity. With the available data on the magnetic resonance of two protons in α- and β-positions, it is possible to derive a difference equation in which the factors b and c vanish. Having chosen an appropriate pair of compounds, it is also possible to write yet another difference equation, the combination of which with the previous equation yields a double difference expression, involving only the relation between the factor a and the electronegativity.

A similar idea was developed by Thompson and Davis[44], who suggest that in compounds of the type AB_3, where B is a halogen or an organic radical, the chemical shift depends only on bond polarity and not on the presence of multiple bonds. Therefore the equation for calculations is of the form

$$\delta = a + bX + c\delta_\pi , \qquad (16)$$

where the bond multiplicity δ_π is determined independently. As a result, it is necessary to subtract the term $1.79\delta_\pi$ in order to obtain the polar component of the chemical shift from the measured value of δ.

Very interesting results have been obtained by Muller and Pritchard[45], who established a relation between the quadrupole bond constant in substituted hydrocarbons (CH_3A) as a function of the electronegativity of A and the interatomic distance r_{C-A}:

$$\chi_{C-H} = 22.6X + 40.1r_{C-A} + 5.5 , \qquad (17)$$

The data presented in this section do not exhaust all the results obtained by the application of spectroscopic methods for the determination of the electronegativities of atoms and radicals, but the principal studies carried out in recent years have been examined.

4. The Use of Ionisation Potentials in Quantum-chemical Calculations

Immediately after the development of the thermochemical method for the determination of the electronegativities, Mulliken[46] suggested that atomic ionisation potentials be used to calculate the electronegativity values. According to Mulliken, the arithmetical mean of the ionisation potential and the electron affinity of the atom in the given valence state is a measure of its electronegativity:

$$X \simeq {}^1/_2(I + E) . \qquad (18)$$

In order to convert Mulliken's values into Pauling's electronegativities, it is necessary to divide the former by a constant (for example 3.27, according to Pilcher and Skinner[47]).

Mulliken's method has been justified quantum-chemically both by Mulliken himself[48] and in Moffit's work[49,50]. Having written the wave function for the bond A–B in the form of a superposition of the wave functions for the purely ionic and purely covalent bonds between the same atoms, Moffit varied the coefficients of these terms in a way which ensured that the condition for formation of a non-polar bond is maintained. Assuming further that the energy of the atomic orbital is approximately equal to the ionisation potential of the corresponding electron and that the difference between the energy of the orbital and the coulombic integral is equal to the electron affinity, he arrived at Eqn. (18) as a measure of the electronegativities of atoms A and B.

The most interesting feature of Mulliken's method is the possibility of calculating the electronegativities of atoms in various valence states and for various degrees of hybridisation. In fact both the ionisation potential and the electron affinity depend significantly on the orbital where the relevant electron is located. Hence it is possible to solve also the converse problem—to determine the degree of hybridisation of the atom in a given compound from the known electronegativity (for example, the thermochemical value) and the known electronegativity values for various orbitals.

Skinner and Summer[51] found by Mulliken's method that the electronegativity of copper is 1.36 in the s-state and 3.32 in the d-state. Using the thermochemical electronegativity of copper, they calculated that in the given case copper is present to the extent of 23% in the d-state. Similar calculations have also been made for nickel.

Later Pilcher and Skinner[47] calculated the Mulliken electronegativities for atoms of the Second Period of Mendeleev's Table in various hybridisation states, which are in good agreement with the electronegativities for single and multiple bonds derived by other procedures. Table 2 presents the corresponding data converted into Pauling electronegativities.

Table 2. Effect of hybridisation on atomic electronegativities.

Element	Orbitals				
	p	sp^3	sp^2	sp	s
Be	—	—	—	1.43	—
B	—	—	1.91	—	—
C	—	2.50	2.74	3.20	—
N	2.46	3.51	3.74	4.40	—
O	3.32	4.66	—	—	2.19

A significant advance in the development of an ionisation method for the determination of electronegativities was made by Iczkowski and Margrave[52], who drew attention to the fact that the ionisation energy of the atom can be represented as a function of the charge:

$$I(q) = aq + bq^2 + cq^3 + \ldots , \qquad (19)$$

where a, b, c, ... are coefficients and q is the number of electrons in the valence shell. However, in practice only the first two terms need be retained in Eqn. (19). Differentiation of this equation with respect to q leads to the formula

$$\frac{\partial I}{\partial q} = a + 2bq . \qquad (20)$$

After substituting $q = 1$ and $q = 2$ in Eqn. (20), one obtains (see Iczkowski and Margrave[52] and Klopman[53])

$$\left(\frac{\partial I}{\partial q}\right)_{q=1} = \frac{I_v + E_v}{2} . \qquad (18a)$$

Thus Iczkowski and Margrave's hypothesis that the electronegativity is a derivative of the energy with respect to charge leads to Mulliken's formula.

Iczkowski's paper was followed by a series of papers by Hinze and Jaffe[54–56], in which the electronegativities were also determined as $\partial I/\partial q$ and the ionisation energies themselves were calculated for the given valence state quantum-chemically using the experimental or interpolated ionisation potentials for the ground state. A significant feature

of these studies is the fundamental approach to the concept of electronegativity not as a property of an abstract atom but as a property of its concrete electronic orbitals in the given chemical compound. The authors introduce the concept of "orbital electronegativity" (OEO) which characterises the capacity of an atom in a molecule to attract an electron to the given orbital. Hence it is clear that orbital electronegativity is a derivative of the energy of the atom and depends on the number of electrons in the orbital.

It is readily seen that this definition is based on two assumptions: (1) that the number of electrons in the orbital can be arbitrary in the range 0–2, including non-integral values; (2) that the energy is a continuous and differentiable (with respect to q) function. To justify both assumptions, one may refer to the experimentally determined distribution of electrons among the bonds joining atoms in molecules and crystals which leads to fractional charges on the atoms in the case of polar bonds. Another test of these assumptions can be provided by the similarity of the electronegativities calculated in this way to the values determined by independent methods.

Table 3. Group electronegativities according to Hinze and Jaffe.

Group R	R (–R)	R (–F)	R (–H)	Group R	R (–R)	R (–F)	R (–H)
CH_3	2.30	1.93	2.33	NH_2	2.82	2.61	2.96
CH_2Cl	2.47	2.13	2.55	PH_2	2.06	1.76	2.04
$CHCl_2$	2.63	2.32	2.77	OH	3.53	3.45	3.82
CCl_3	2.79	2.50	2.98	SH	2.35	2.11	2.38

The possibility of the determination of group electronegativities by the Hinze–Jaffe method is also very important[55]. These values are calculated on the assumption of a certain degree of hybridisation and polarity of the bond in radicals. Hence it follows immediately that the group electronegativity will depend to a high degree on the atom or radical with which the given group is linked. To characterise this effect, Table 3 lists the group electronegativities for covalent radicals (i.e. for radicals linked to groups of precisely the same kind) and for radicals combined with hydrogen and fluorine. Table 3 shows that the trend in the changes of the electronegativity values for radicals remains constant in all three cases but, if one includes, for example, hydrogen ($X = 2.20$) in this series of radicals, then it is readily seen that its relative position will differ appreciably depending on the atom with which it is combined. We shall return to this problem later.

The use of ionisation potentials for the calculation of electronegativities appears to be a very attractive procedure and this is in fact widely done by various investigators. Of the work of Soviet investigators, one should mention the studies of Nekrasov[57] and Povarennykh[58] and concerning the work of non-Soviet scientists one may refer to Chang's study[59], wherein an extensive calculation was made of the electronegativities of atoms in various states of hybridisation from formulae genetically related to Mulliken's equation. It must, however, be pointed out that ionisation potentials have to be used very cautiously, taking into account the peculiarities of this property. Thus, in an attempt to calculate the ionisation electronegativities of radicals, Pritchard and Skinner[8] used the values of I and E for the ground state and the same conversion factor as for the atomic ionisation potentials in the valence state. According to the data of Hinze and Jaffe, the equation relating the Mulliken electronegativities to Pauling's values is of the form

$$X_P = 0.336(X_M - 0.615) \quad (21)$$

On the other hand, if the ionisation potentials for the ground state are used, the formula is somewhat different:

$$X_P = 0.4(X_M - 0.5) \quad (22)$$

However, even the use of Eqn. (22) does not save the situation. The reason is that the ionisation potential and the electron affinity of a radical are essentially determined for different components, i.e. different atoms. As a simplification, one can of course postulate that the first ionisation potential of the radical corresponds to the removal of an electron from the negatively charged component. Similarly the electron affinity of the radical corresponds to the addition of an electron to the positively charged component. Consequently we are not justified in combining the ionisation potential determined for the radical with its electron affinity. Eqn. (18) can be used only when we can determine for the same atom in the radical both the ionisation potential and the electron affinity.

So far Mulliken's method can be applied to covalent molecules of the type A_2, where the above indeterminacy does not exist. The present author believes that the best way of applying Mulliken's method to molecular problems consists in comparing the sum of ionisation potentials and electron affinities for the molecules and the isolated atoms and then introducing corrections to the standard electronegativity on the basis of this comparison[60,61]. It has been shown[4] that the electronegativity of an isolated A atom is higher by 20% than the value in the molecule A_2. The reason for the increase of electronegativity on going from a covalently linked atom to a free atom consists precisely in the presence of the free valence, which leads to an additional energy gain on formation of the bond due to the electron pairing energy.

Similarly it proved possible to determine also atomic electronegativities for aqueous solutions[62] (Table 4). It is interesting that the electronegativities of metals are sharply reduced as a result of the hydration of the cations in aqueous solutions (Table 4).

Using the ionisation potentials and electron affinities of the carbon atom in various states of hybridisation, it proved possible to show[4] that $X_{C=} = 2.0$, $X_{=C-} = 2.8$, and $X_{\equiv C-} = 3.1$, i.e. to obtain a result similar to that derived by all other methods for the determination of electronegativities.

5. Compilation of Electronegativities

The above data show that the electronegativity of an atom depends on its valence, state and degree of hybridisation of its bonds, and even on the medium in which the given molecule is located. However, this is a characteristic feature of many concepts in structural chemistry. For example, the concept of the atomic radius was initially formulated by Bragg as a constant for a given element. Then the radii were differentiated into ionic and covalent, metallic and van der Waals. Within each Group relations were subsequently established between the radii and the valence of the atom, its coordination number, or bond multiplicity; molecular radii for ions in aqueous solutions have been derived.

Table 4. Electronegativities of the elements in aqueous solutions.

Group / Period	1a	2a	3a	4a	7a	8a	1b	2b	3b	4b	6b	7b
I	H 0.32											
II	Li 0	Be 0.13										F 3.87
III	Na 0.11	Mg 0.17							Al 0.18		S 2.28	Cl 3.15
IV	K 0.06	Ca 0.09	Sc 0.14	Ti 3+ 0.16	Mn 2+ 0.18	Fe 2+ 0.28 3+ 0.35 Co 2+0.28 Ni 2+0.34	Cu 1+ 0.32	Zn 0.38	Ga 0.25			Br 2.71
V	Rb 0.04	Sr 0.08	Y 0.07				Ag 0.55	Cd 0.46	In 0.31	Sn 2+ 0.44		I 2.34
VI	Cs 0.02	Ba 0.06	La 0.06					Hg 0.56	Tl 0.44	Pb 2+ 0.41		
VII		Ra 0.09										

Although this procedure increases our information about the structure of matter, this type of development of a concept reflects the fact that a molecule or a crystal is regarded as approximately a collection of interacting atoms. In a more rigorous approach, where the molecule or a crystal is regarded as a single system, a collection of nuclei and electrons, all the additive concepts of structural chemistry vanish altogether. Therefore a rigorous solution of the many-electron problem is impossible: in practice investigators use the "atoms in the molecule" method and then all that has been said above is valid.

The methods for the determination of electronegativities discussed in Sections 1–4 yield values characterised by different dimensions, which is undesirable for a physical concept. This disturbs some investigators (see, for example, Iczkowski and Margrave[52]) and can lead to misunderstanding of the role and position of the concept of electronegativity in the treatment of the nature of the chemical bond. The point, however, is that the concept of electronegativity is chemical in nature, reflecting one of the aspects of the chemical bond and therefore it cannot be characterised, in principle, by only one physical dimension. Chemical combination of atoms leads to a change in size, energy, and spectroscopic, magnetic, electrical, and other properties of the elements and can be adequately expressed in terms of these properties. However, it is evident that none of the properties enumerated above can exhaustively describe all the specific features of the reaction, the entire chemistry of the phenomenon. One can assert that a wide variety of dimensions of the concept is encountered not only with electronegativities but also with any other chemical concept. This can be demonstrated by examining the possible quantitative characteristics of the dimensions of such concepts as "metal", "hydrogen bond", "acid", "reactivity", etc.

Table 5‡ presents a compilation of the electronegativities of the elements, which can be recommended at the present time on the basis of the results obtained by different methods. Table 6 lists examples of the effect of bond multiplicity on atomic electronegativities.

‡ For hydrogen, antimony, and the actinides, the upper rows correspond to the lower-oxide state, and the lower rows to the higher-oxide state.

The same values can be used for an approximate calculation of the electronegativities of other atoms with multiple bonds, as can be seen in Table 7, where the electronegativities of molecular radicals are compiled. These are the electronegativities of the atoms in the radicals which are combined with the remainder of the molecule, for example, oxygen in NO_3 or nitrogen in NO_2. In compiling Table 7, the data of Ettinger[63] and Huheey[64] were used in addition to those quoted earlier.

In conclusion of this Section, we can consider briefly the problem of the electronegativities of the inert gas atoms. The problem of the calculation of these quantities arose after the publication of work on the fluorides and oxides of the inert gases and therefore the first electronegativities of inert gases were calculated (by Mulliken's method) as late as 1963 by Neiding[65] and Rundle[66]. The data of Sanderson[28] and Fung[67], obtained by means of different methods, are more correct. These values are in fact used in Table 5. Sanderson made the significant remark that the electronegativities of the inert gases must be understood not as the oxidising capacity of the elements but as the capacity of the atoms to resist the removal of their electrons on formation of a polar bond.

III. THE SCOPE OF THE APPLICATION OF THE CONCEPT OF ELECTRONEGATIVITY

As already stated above, any of the methods of calculation can be used to apply electronegativities. In this section we shall examine the use of the concept of electronegativity in the treatment of chemical properties only of substances (mainly inorganic) and various manifestations of the nature of the chemical bond in molecules and crystals. However, before presenting the factual data, several preliminary comments must be made.

The concept of electronegativity is not a theory in the sense that it does not explain experimental findings on the basis of some new hypotheses. It permits only the estimate or measurement of the asymmetry of the electron cloud of the bond, i.e. it makes it possible to say which of the species involved in the bond has a negative and which a positive charge and what is the approximate magnitude of these charges. Having obtained such information, the investigator can set up (on the basis of a familiar theory or

Table 5. Electronegativities of the elements.

1a	2a	3a	4a	5a	6a	7a	8a	1b	2b	3b	4b	5b	6b	7b	8b
														H 2.2	He 2.8
Li 1.0	Be 1.6									B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne 4.4
Na 0.9	Mg 1.2									Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar 3.5
K 0.8	Ca 1.0	Sc 1.3	Ti II 1.4 IV 1.6	V III 1.5 IV 1.7 V 1.9	Cr II 1.5 III 1.6 VI 2.4	Mn II 1.4 III 1.5 IV 2.1 VII 2.5	Fe II 1.8 III 1.9	Co 1.8	Ni 1.9	Cu I 1.8 II 2.0	Zn 1.6	Ga 1.7	Ge 2.0	As 2.1	Se 2.5	Br 3.0	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr II 1.3 IV 1.5	Nb 1.6	Mo IV 1.7 VI 2.3	Tc V 1.9 VII 2.3	Ru III 2.0 IV 2.1	Rh 2.1	Pd 2.1	Ag 1.9	Cd 1.7	In 1.8	Sn II 1.8 IV 2.0	Sb 1.9 2.2	Te 2.3	I 2.6	Xe 2.6
Cs 0.7	Ba 0.9	La 1.1	Hf 1.4	Ta 1.5	W IV 1.6 VI 2.2	Re V 1.9 VII 2.1	Os III 2.0 IV 2.1 VIII 2.4	Ir 2.1	Pt II 2.1 IV 2.2 VI 2.6	Au 2.3	Hg 2.0	Tl 1.4 1.9	Pb II 1.9 IV 2.1	Bi III 2.0 V 2.2	Po 2.2	At 2.3	Rn 2.3
Fr 0.7	Ra 0.9	Ac 1.1															

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
lanthanides	1.1	1.1	1.2	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.2

	Th	Pa	U	Np	Pu → Cf
actinides	1.2 1.5	1.3 1.7	1.4 1.8	1.4 1.9	1.3

Table 6. Effect of bond multiplicity.

Bond type	X	Bond type	X
C—	2.6	(—C)—	2.6
C⋯	2.3	(⋯C)—	2.7
C=	2.2	(=C)—	2.8
C≡	2.1	(≡C)—	3.2

Table 7. Electronegativities of molecular radicals.

Radical	X	Radical	X	Radical	X
CF_3	3.1	NF_2	3.4	PO_3	3.4
CCl_3	2.8	NC	3.3	BO_3	3.4
CBr_3	2.7	NO_2	3.2	SO_3	3.5
Cl_3	2.6	N_3	3.2	CO_3	3.6
CH_3	2.5	NCS	3.1	NO_3	3.8
C_2H_5	2.6	SCN	2.8	PO_4	3.6
C_6H_5	2.8	NH_2	3.0	SO_4	3.7
$CH=CH_2$	2.9	PH_2	2.2	ClO_4	3.9
C≡CH	3.3	OH	3.5		
CHO	2.9	SH	2.6		
COOH	3.0	SeH	2.4		
CN	3.3				

relation) a hypothesis concerning the law governing the variation of the chosen physicochemical property of the substance as a function of the polarity of its bond. Thus, for a successful application of the concept of electronegativity, it is necessary to know how the ionic character of the chemical bond influences a given characteristic and only then introduce quantitative criteria.

The above limitations do not diminish the scope of the concept of electronegativity, since millions of molecules and crystals have structures involving polar bonds and the total number representatives of extreme types of bonds in nature amounts to only several hundred. Therefore the study of polar bonds is of great theoretical and practical importance.

1. Atomic Charges in Molecules and Crystals

Even simple comparison of the electronegativities of two atoms makes it possible to say which of them will behave as an electron donor or acceptor on formation of the bond. However, additional theoretical and experimental data must be used to establish a quantitative relation.

The first functional relation between the ionic bond and the difference between atomic electronegativities was established by Pauling[68] in 1939. Having adopted as the reference points the effective atomic charges in hydrogen halide molecules, calculated from the simple formula

$$i = \frac{\text{dipole moment}}{\text{bond length}} \qquad (23)$$

and the thermochemical electronegativities, he obtained a smooth curve, which fits the following equation:

$$i = 1 - e^{-0.25\Delta X^2}. \qquad (24)$$

After the dipole moment of hydrogen fluoride had been corrected, Pauling modified Eqn. (24):

$$i = 1 - e^{-0.18\Delta X^2}. \qquad (25)$$

Table 8 lists the values calculated by this formula.

The validity of Eqn. (25) has been confirmed theoretically by many investigators (see the present author's monograph[4] for a more detailed description), who obtained by independent methods similar values for the ionic character of hydrogen halide molecules and certain other simple cases. It is significant that even the most accurate atomic charges obtained by Barinskii and Nadzhakov[70] by X-ray spectroscopy are also in fairly good agreement with Pauling's data. The experimental percentages of the ionic character of the bonds§ are listed below (first row) together with the theoretical values (second row) obtained from a comparison of the data in Tables 5 and 8.

CS_2	GeH_4	H_2S	$GeBr_4$	IBr	HCl	$ZnBr_2$
0	5	5	17	10	20	25
0	2	5	20	5	20	32 .

§ Calculated from the atomic charges.

Chronologically the next important study on the use of electronegativities for the calculation of the ionic character of bonds in molecules is that of Sanderson[26-28]. According to Sanderson, the stability ratio (i.e. the electronegativity in his terminology) of any atom in a molecule is equal to the stability ratios of all the remaining atoms, i.e. on formation of the bond the stability ratios of the atoms become equalised. This postulate is almost self-evident, since it is clear that in a stable molecule or bond the electron pair will be located at such a distance from each species involved that the attraction which it exerts is balanced out and this means that the stability ratios are equalised. Sanderson suggests that in practice the geometrical mean stability ratio be calculated as the value for the molecule AB:

$$SR_{AB} = \sqrt{SR_A \times SR_B}\,. \qquad (26)$$

Table 8. Dependence of the ionic character of the bond in molecules on electronegativity.

ΔX	i	ΔX	i	ΔX	i	ΔX	i	ΔX	i	ΔX	i
0.0	0	0.5	7	1.0	20	1.5	35	2.0	51	3.0	80
0.1	1	0.6	9	1.1	23	1.6	38	2.2	58	3.2	84
0.2	2	0.7	11	1.2	26	1.7	41	2.4	64	3.4	88
0.3	3	0.8	14	1.3	29	1.8	44	2.6	70	3.6	91
0.4	5	0.9	17	1.4	32	1.9	47	2.8	75	3.8	93

Having further postulated that the ionic character of the bond in the sodium fluoride molecule amounts to 75%, Sanderson was able to calculate the ionic electronegativities of the sodium and fluorine atoms and then of all the remaining elements in the Periodic System. When the set of covalent and ionic stability ratios is available, it is easy to calculate the ionic character of the bond from the equation

$$i = \frac{SR_{AB} - SR_{A^0}}{SR_{A^+} - SR_{A^0}}\,. \qquad (27)$$

Comparison of the values of the ionic character of the bond obtained by Sanderson's and Pauling's methods shows that the average statistical discrepancy amounts to 10%.

However, extension of Sanderson's method to more complex compounds (including complexes) leads to incorrect results[71]. This is reasonable, since, for example, in potassium sulphate there are two independent (to a first approximation) bond systems, K–O and S–O, and there is no need for the requirements that the stability ratios of the potassium and sulphur atoms should be equalised on formation of this compound.

The present author proposed a modification of Sanderson's method, based on the postulate that the electronegativity of an atom is a characteristic of one valence state[72] (see also Iczkowski and Margrave's definition of electronegativity). Therefore the method of calculating the stability ratio for a compound was modified so that under the root sign the stability ratios of the species involved in the bond were each raised to a power equal to the product of the valence of the atom and the number of such atoms in the given molecule:

$$SR_{A_nB_m} = \sqrt[np+mk]{SR_A^{np} \times SR_B^{mk}}\,, \qquad (28)$$

where p is the valence of atom A, k the valence of atom B, and n and m are the numbers of atoms A and B in the molecule respectively. Since in neutral molecules $np = mk$, Eqn. (28) transforms into

$$SR_{A_nB_m} = \sqrt{SR_A \times SR_B}\,. \qquad (29)$$

Thus on formation of any complex molecule only the stability ratios of linked atoms are equalised and the stability ratio of the molecule must be equal to the geometrical mean of the values for the species involved in the chemical bonds.

The suggested modification of the method makes it possible to avoid the contradictions which arose in the calculation of the stability ratios of molecules containing polyvalent atoms. For example, according to Sanderson the stability ratio of the sodium atom in Na_2O is less than in sodium itself and therefore the ionic character in the first case is lower than in the second, which is incorrect. Sanderson's modified method can also be applied in the calculation of the stability ratios of complex ions, for example the sulphate ion:

$$SR_{SO_4} = \sqrt[7]{SR_S^3 \times SR_O^4}\,. \qquad (30)$$

On comparing the stability ratio of the sulphur atom in the sulphate ion with the values for neutral and positively charged sulphur, it is readily seen that $SR_{SO_4} = 4.48$ corresponds to a charge of +0.15 on the sulphur atom. The stability ratios of a number of oxygen-containing anions, listed in Table 9 together with the charges of their central atoms, were calculated similarly. Comparison of the data in Tables 7 and 9 shows that the sequences of experimental and theoretically calculated electronegativities of radicals are the same.

Table 9. Stability ratios (SR) and charges (Z) of atoms in complex ions.

Ion	SR	Z for central atom	Ion	SR	Z for central atom
BO_3^{3-}	4.05	+0.42	SeO_4^{2-}	4.63	+0.11
CO_3^{2-}	4.49	0.17	TeO_4^{2-}	4.28	0.21
NO_3^-	4.86	0.04	CrO_4^{2-}	4.30	0.20
VO_3^-	4.15	0.22	MoO_4^{2-}	4.19	0.24
ClO_3^-	4.91	0.03	WO_4^{2-}	4.74	0.08
BrO_3^-	4.79	0.06	ClO_4^-	4.91	0.03
IO_3^-	4.44	0.15	BrO_4^-	4.78	0.06
SiO_4^{4-}	3.82	0.82	IO_4^-	4.43	0.15
PO_4^{3-}	4.10	0.32	MnO_4^-	4.28	0.18
AsO_4^{3-}	4.42	0.23	ReO_4^-	4.99	0.01

A procedure for the determination of the ionic character of the bond, similar to Sanderson's method, was developed by Lakatos[73-75], who suggested that, on formation of the molecule AB, the forces which the effective charges of the nuclei of the atoms A and B exert on the valence electrons should be equalised. This hypothesis enabled Lakatos to obtain results differing on average by 7% from the amounts of ionic character calculated by Pauling's method.

Simultaneously with Lakatos, Fereira[76] used the idea of the equalisation of electronegativities on bond formation. He concentrated particularly on the relation between the electronegativity of the atom and its effective charge q.

Having expressed the electronegativity of the real atom by a power series, as suggested by Daudel[77,78]

$$X(q) = X(0) + a\left(\frac{\partial X}{\partial q}\right) + \cdots \quad (31)$$

and having retained only the first and second terms of the expansion, Fereira was able to calculate, on the basis of the postulated equality of $X_A(q)$ and $X_B(q)$ in the A–B bond, the amounts of ionic character in the bonds of hydrogen halides, in good agreement with Pauling's data: 32% for HF, 16% for HCl, 10% for HBr, and 5% for HI.

The equalisation principle has also been used in the method of orbital electronegativities[79-81]. Since in this method the electronegativity of an atom is also represented by a linear function of the charge, the formulae and the results are very similar to those obtained by Fereira.

The data presented show that Sanderson's idea of the equality of the electronegativities of atoms when these form a stable bond has been widely accepted and has given rise to the possibility of calculating the ionic character of the bonds in molecules, the result being in qualitative or even semiquantitative agreement with experiment. It is only fair to mention that Sanderson's postulate originates from the fundamental work of Pauling[68], who established that, when an atom acquires a positive charge, its electronegativity increases (approximately by 0.4 for each +1 unit of charge) and on acquisition of a negative charge it decreases to the same extent. As a result, on formation of a polar bond, the electronegativity of the cationic component of the molecule increases and that of the anionic component falls, i.e. the electronegativities of the two atoms approach one another. The electronegativity increments quoted by Pauling for ± 1 units of charge are, of course, approximate and corrected values will be given below: here it is desired to mention only the fundamental aspect of the problem.

The approach to the determination of the ionic character of bonds in molecules examined above has been criticised by Pearson and Gray[82], who remarked that the equalisation of electronegativities only reduces the mutual electrostatic energy and the change in the overlapping of the wave functions is not taken into account. However, the Coulombic component of the energy of polar bonds is the major component of the total bond energy and therefore the above approximation is in practice quite acceptable. Pritchard[83] took into account the effect of the change in the overlapping of the orbitals for the carbon–nitrogen bond and showed that the electronegativities of the atoms are not then equalised but their values approach one another—after the formation of the bond the difference between the electronegativities of the species in the bond amounts to only 10% of ΔX for these atoms before interaction. This calculation yields a characteristic estimate of the degree of approximation in the "electronegativity equalisation" method.

The ionic character of the bond can be calculated also with the aid of overlap integrals (OI). The latter characterise the electron density of the bond and in a series of similar molecules vary quite steadily, namely the overlap integral decreases with increasing ΔX, i.e. bond polarity. However, for a quantitative solution of the problem, it was necessary to normalise the overlap integrals, i.e. to adjust them to a single scale. For this purpose, the present author suggested[21,84,85] that the overlap integral of a real bond A–B be compared with the overlap integral of a purely covalent bond between the same atoms, the latter being defined as a bond whose length is equal to the sum of the covalent radii and whose polarity is zero (the second condition means that the effective charges quoted for the atoms A and B are equal). Then the ratio of the overlap integrals of the real and purely covalent bonds represents the covalent character of the bond A–B. Calculations showed that the results are close to Pauling's data and are described by the same equation:

$$i = 1 - e^{-0.25\Delta X^2}. \quad (32)$$

We now come to the description of methods in which empirical data are used, the reader being referred to the present author's monograph[4] where other theoretical studies on the calculation of the ionic character of ionic bonds in molecules carried out up to 1960 are described. The first method using experimental data for the calculation of the ionic character is that of dipole moments [see Eqn. (23)]. Later it was shown that the dipole moment is a complex function which depends on the ionic character and hybridisation of bonds and also on the effect of isolated electron pairs.

At the present time these other factors cannot be taken into account although certain advances on those lines have been made[86]. Therefore the employment of dipole moment data can be justified only in those cases where all the factors, except the ionic character of the bond, are low or cancel out. This condition obtains in hydrogen halides.

The application of radiospectroscopic data, for example data on quadrupole interaction, which appeared very promising initially, later failed to justify these hopes, since for an unambiguous determination of the ionic character of the bond it is again necessary to know accurately the degree of hybridisation of the bond. In those cases where the latter characteristic is unknown, certain assumptions are made concerning the type and degree of hybridisation[4] and therefore the final data are of no greater value than the initial assumptions. Data on quadrupole interaction can be used directly only for qualitative purposes in comparing similar or genetically related molecules. Fundamentally important results were obtained recently by Mikhailov[87,88] and Gilson[89], who used orbital electronegativities to establish a relation between the ionic character of the bond and the quadrupole coupling constant χ. Since orbital electronegativities are themselves functions of bond hybridisation, it is possible to establish more unambiguous relations between χ and the ionic character of the bond.

A third method whereby experimental data are used to calculate the degree of ionic character of the bond is based on chemical bond energies. The principal idea of this procedure consists in the representation of the bond energy by a set of ionic and covalent terms (supplemented by a polarisation component or account being taken of bond multiplicity). On minimising such a system by the variation of the relative contributions of both terms or by comparing the calculated and experimental values, it is possible to obtain information about the ionic character of chemical bonds. In an elementary form this idea is contained even in Pauling's basic equation [Eqn. (1)] and subsequently only the calculation of the two terms of bond energy was formulated in a concrete form. In the author's monograph[4] the covalent component of bond energy was calculated with the aid of overlap integrals, while Pearson and Gray[82] used the Coulombic and exchange integrals, for complex molecules the latter being calculated with the aid of empirical data on covalent bond energies and ionisation potentials.

In a series of studies by Fereira[90-92] the ionic character of the bond was calculated by the equation

$$E(A-B) = E_{cov} + E_{coul} + \Delta E_A(q) + \Delta I_B(q), \quad (33)$$

where ΔE and ΔI are the partial electron affinity and partial ionisation potential. These concepts reflect the energies

which must be expended to remove "part of the electron" (in the statistical meaning of this term) or which are evolved on partial addition of the electron to the atom. Subsequently Fereira modified the first two terms of Eqn. (33), namely he established a relation between the covalent energy term and the ionic character of the bond, took account of hybridisation, and varied not only the polarity but also the chemical bond length in order to minimise the energy.

The energy method can be applied, however, only in simple cases—di- or tri-atomic molecules. In more complex molecules it is difficult to take into account the non-valence interatomic interaction and bond hybridisation. This is the reason why it is almost impossible to calculate the ionic character of the bond. Therefore, for fairly complex systems, the only suitable experimental method available at the present time is X-ray spectroscopy. Table 10 compares the results of X-ray spectroscopic studies on the molecules of ferrocene and its analogues[93-95], with the values calculated by the present author[96] using the electronegativity method.

Table 10. Effective atomic charges in π-complexes.

Molecule	X-ray spectrum		EO method	Molecule	X-ray spectrum		EO method
	Refs.93 and 94	Ref.95			Refs.93 and 94	Ref.95	
Fe $(C_5H_5)_2$	0.4	0.73	0.70	Ni $(C_5H_5)_2$	—	0.65	0.55
Fe $(C_5H_5)_2^+$	—	0.68	0.76	Ni $(C_5H_5)_2^+$	1.0	—	0.76
Co $(C_5H_5)_2$	0.4	—	0.70	Mn $(C_5H_5)_2$	1.5	1.6	1.25
Co $(C_5H_5)_2^+$	1.2	0.8	0.94	Cr $(C_6H_6)_2$	1.1	1.5	1.44

It follows from Table 10 that the electronegativity method can be used to describe the distribution of charges in molecules, in good agreement with experiment.

Before concluding the description of the methods of calculating charges in molecules, we must return to the question of taking into account the effect of bond polarities on atomic electronegativities. When a molecule of the type MA_2 formed by the combination of atoms M and A, the latter acquire charges i due to the ionic character of the bond. The appearance of a positive charge i increases the electronegativity while the appearance of a negative charge reduces it. As a result, in order to calculate the ionic character of the second M–A bond it is necessary to compare the electronegativity of the atom A with $X_M + ip$, where p is a constant coefficient equal to the change in X on appearance of an integral charge. Bearing in mind the equivalence of both M–A bonds in MA_2 molecules, the ionic characters of the first and second M–A bonds must be averaged. This is the general scheme of the calculation of the ionic character of the bonds in complex molecules (for other examples, see the monograph[4]).

The coefficient p can be determined using Eqn. (6). For this purpose, a variable value of the atomic radius, varying as a result of ionisation (see the author's monograph[4], p. 176), must be substituted in the formula

$$X = a\frac{Z^*}{r} + 0.54 . \qquad (6)$$

and Z^* must be changed appropriately as a function of i. Calculations for all the electropositive elements of the Periodic System show that $p = 0.4$ for Periods III–VI and $p = 0.8$ for the elements of Period II. For the electronegative elements, $p = 0.4$ (chalcogens) and $p = 0.8$ (halogens). Thus the value $p = 0.4$ postulated by Pauling has been confirmed in general. However, fundamentally different results are obtained for hydrogen. The formula for the calculation of X_H is of the form

$$X = 0.60\frac{Z^*}{r} + 0.54 . \qquad (6)$$

Assuming that the radius of the hydrogen atom varies according to the same law as for divalent cations (see Ref. 97), it is easy to calculate that the electronegativity increases anomalously with increasing charge:

Charge =	0	+0.1	+0.2	+0.3	+0.4	+0.5 ...
X=	2.1	2.5	3.0	3.6	4.4	5.6 .

Hence it follows that, after the formation of a bond, for example C–H, where the hydrogen atom should acquire a charge of +0.06, the electronegativity of hydrogen increases to 2.4, i.e. significantly approaches the electronegativity of the methyl group. If, as a result of the mutual influence of the atoms in substituted hydrocarbons, the ionic character of the C–H bond increases still further, the relative electronegativities of the carbon and hydrogen atoms may be reversed. This may explain the unusual finding that in many hydrocarbons the methyl group frequently behaves as a more powerful electron donor than hydrogen. This anomalous variation of the electronegativity of the hydrogen atom with increasing positive charge can also constitute the basis for explaining the contradictions which occur in the determination of the direction of the moment in the C–H bond.

Coming now to the determination of the ionic character of bonds in solids, the following fundamental characteristics of the coordination crystals of inorganic compounds must be emphasised: namely the valence of the atoms is as a rule less than the coordination number (CN). If, for simplicity, we consider sodium chloride, it is evident that in the crystalline state, where each sodium atom is surrounded by six chlorine atoms, there can exist only one normal NaCl chemical bond because the Na and Cl atoms are univalent, and the interaction between the sodium ion and the remaining five chloride ions can only be of the Coulombic, ion–dipole type. The ionic character of such an electrostatic bond, i.e. the degree of ion–dipole interaction, can be conveniently calculated by a formula similar to that proposed by Nekrasov[57]:

$$i_{\text{el-stat.}} = \frac{I_B - X_A}{I_B + X_A} . \qquad (34)$$

This formula reflects the relative effects of two forces on the electron cloud of the atom B (in the present case Cl)—its attraction by the atom A (in our case Na), characterised by its electronegativity, and the resistance by the atom B to the withdrawal of electrons, characterised by its ionisation potential.

Since in fact all six Na–Cl bonds within the coordination polyhedron are equivalent, the ionic characters of the electrostatic and the normal chemical bonds must be averaged:

$$i_{\text{cryst}} = \frac{i_{\text{mol}} + (\text{CN} - 1)\, i_{\text{el-stat}}}{\text{CN}} . \qquad (35)$$

In the more general case of compounds consisting of polyvalent atoms we have

$$i_{\text{cryst}} = \frac{i_{\text{mol}} + (\text{CN} - Z)\, i_{\text{el-stat}}}{\text{CN}} , \qquad (36)$$

where Z is the valence. In Eqns. (35) and (36) i_{mol} denotes the ionic character of the bond determined from a comparison of the electronegativities of the atoms, i.e. in the same way as for molecules.

The formulae proposed for the calculation of the ionic character are of course approximate, in particular where account of the polarisation ion–dipole interaction is concerned. Their validity may be assessed by comparing the calculated data with experimental results. For the latter, we used the results obtained by Szigeti's method, by X-ray spectroscopic investigation of crystals, and from thermochemical data for crystalline compounds.

Without dwelling on the theory of Szigeti's method, we shall quote at once the final formula whereby it is possible to calculate the effective charge per bond, i.e. the ionic character of the bond expressed in terms of fractions of an electron:

$$(e^*)^2 = \frac{\pi(\varepsilon - n^2)\cdot \mathrm{M}\,\omega_0^2}{\left(\frac{n^2+2}{3}\right)^2 (Ze)^2 N_a}, \qquad (37)$$

where e^* is the effective charge of the atom (divided by the valence Z) in terms of fractions of the electron, n the refractive index, ϵ the dielectric constant, M the reduced mass of the pair of atoms M–A, M the absolute mass of the atoms, N_a the number of molecules (more precisely the number of formula units per cm^3, and ω_0 the frequency of lattice vibrations. In some cases (for crystals of the type MA_n) the present author's data differ from the literature values[98–100] because the reduced mass is expressed throughout in the form

$$\mathrm{M} = \frac{M_A\ M_B}{M_A + M_B}, \qquad (38)$$

as is done in spectroscopy (see also Refs. 101 and 102).

Table 11. Comparison of effective charges determined by Szigeti's method (e^*) and by the electronegativity method (i).

Crystal	e^*	i	Crystal	e^*	i	Crystal	e^*	i
LiCl	0.73	0.81	AgCl	0.71	0.66	InAs	0.19	0.19
LiBr	0.68	0.79	AgBr	0.66	0.63	InSb	0.11	0.17
NaBr	0.70	0.80	TlCl	0.80	0.76	Gd_2O_3	0.71	0.70
NaI	0.71	0.77	TlBr	0.82	0.73	Y_2O_3	0.66	0.70
KF	0.96	0.90	BeO	0.63	0.62	Ho_2O_3	0.68	0.70
KCl	0.81	0.84	MgO	0.73	0,75	Er_2O_3	0.66	0.70
KBr	0.78	0.81	CaO	0.75	0.78	Tu_2O_3	0.76	0.70
KI	0.71	0.79	SrO	0.75	0.78	Yb_2O_3	0.74	0.72
RbF	0.93	0.90	ZnO	0.58	0.62	Lu_2O_3	0.73	0.70
RbCl	0.87	0.85	ZnS	0.52	0.46	Y_2O_3	0.73	0.70
RbBr	0.84	0.82	BN	0.38	0 32	CaF_2	0.82	0.86
RbI	0.81	0.79	AlSb	0.16	0.19	SrF_2	0.85	0.86
CsF	0.88	0.91	GaP	0.19	0.23	BaF_2	0.87	0.87
CsCl	0.85	0.86	GaAs	0.14	0.21	EuF_2	0.84	0.84
CsBr	0.78	0.84	GaSb	0.10	0.18	TiO_2	0.56	0.54
CsI	0,74	0.81	InP	0.20	0.21	SiO_2	0.37	0.35

The amounts of ionic character (in fractions of the electron) determined by the electronegativity method were found from Eqn. (36) and from Tables 5 and 8; the values of the ionic character of electrostatic bonds were taken from the present author's monograph[4]. Table 11 shows that the agreement between the theoretical and experimental values of the ionic character of the bond is on average to within 4%.

The next most accurate method for the determination for atomic charges in crystalline compounds is X-ray spectroscopy. Here two different approaches have been formulated. In one of them (see the work of Urusov[103] and Nefedov[104]) the shift of X-ray lines on ionisation of atoms is examined and a relation is established by quantum-chemical methods between the magnitude of the shift and the effective charge. The above workers do not specify to what type of charges their values refer, but it is evident from the considerations developed in their papers and the normalisation employed[105] that the charges obtained are of the same type as those which follow from Szigeti's equation and the amounts of ionic character in fractions of the electron are referred to a single valence. The present author believes[4] that such an atomic charge, which is associated with the loss or acquisition of an integral electrostatic charge or a fraction of the latter, can be usefully called the intrinsic atomic charge; the charge is distributed within the limits of the atomic skeleton, i.e. it operates within a sphere described by a radius extending from the nucleus to the outer closed electronic orbitals. Suchet[106] suggests that the intrinsic charges be also called "physical charges".

Apart from the intrinsic atomic charges, it is necessary to introduce the concept of coordination charges which represent the collection of electrons received by the given atom from the atoms in the first coordination sphere and the positive charges acquired by the given atom as a result of losing its valence to the bonds with other atoms[4]. Suchet suggests that such charges be called "chemical charges"[106] (see also Cochran[107]). These verbal formulations are identical with the equations

$$Z^*_{\mathrm{intr}} = iZ;\ Z^*_{\mathrm{coord}} = iZ - (1-i)\mathrm{CN}. \qquad (39)$$

It is evident from these formulae that the intrinsic charge of the atom will be always positive for cations and negative for anions. The effective coordination charge can be of either sign both for cations and anions and in most cases it is small in absolute magnitude (Pauling's electroneutrality rule[108,109]). It is significant that, when the bond has a large proportion of covalent character and the coordination number is likewise large, Z^*_{coord} for metals in compounds can be negative. This problem will be discussed further below.

Table 12. Intrinsic charges of metal atoms in crystals.

Crystal	$Z^*_{\text{X-ray}}$	Z^*_{EO}	Crystal	$Z^*_{\text{X-ray}}$	Z^*_{EO}
MgF_2	1.25	1.62	FeF_2	1.91	1.46
$MgSO_4$	1.15	1.56	$FeSO_4\cdot 7H_2O$	1.78	1.84
$MgCO_3$	1.10	1.52	$FeCl_2\cdot 4H_2O$	1.63	1.74
MgO	1.00	1.50	FeC_2O_4	1.65	1.32
			FeS	0.69	1.02
Al_2O_3	1.15	1.89	FeF_3	1.72—2.23	1.95
$AlCl_3$	1.45	0.71	$Fe(NO_3)_3\cdot 9H_2O$	1.70	1.83
AlP	0.60	0.72	$Fe_2(SO_4)_3\cdot 9H_2O$	1.71	1.77
SiO_2	1.30—1.50	1.40	Fe_2O_3	1.58	1.65
P_2O_5	0.75	1.30	$FeCl_3$	0.90	1.47

The values of Z^*_{intr} calculated with the aid of electronegativities and determined from X-ray spectroscopic data are compared in Table 12.[103,104] It follows from the Table that the average difference between the effective charges amounts to 0.12 per bond. Here one must mention in addition the calculations of charges in iron(II) salt hydrates. It is known from structural analysis that in the crystal structure of such salts the iron atom is surrounded by six water molecules arranged octahedrally, i.e. here the situation is the same as in aqueous solutions of iron salts. According to crystal chemists[110,111], the interatomic distances and the nature of the interaction between ions in aqueous solutions and in hydrates are the same. Therefore in calculations of the ionic character of such hydrates the electronegativities of atoms in aqueous solutions should be used (Table 4).

The results of the calculations of the effective charges of atoms in crystals by Eqn. (39) using electronegativities and Barinskii's data[70,93,94], which he obtained by the X-ray spectroscopic method, are compared in Table 13. This group of investigations was undertaken to study the behaviour of the X-ray electron within the first coordination sphere. Calculation of the size of the sphere in which the electron moves leads to a value which is intermediate between the ionic and covalent radii of the metal studied by the X-ray spectroscopic method, which demonstrates the dependence of the behaviour of the electron precisely on the effective charge. This finding was mentioned earlier[4] and was again demonstrated recently in the dependence of the position of the edges of the absorption X-ray K-spectra of manganese on the effective and not on the intrinsic atomic charge in crystalline compounds[112].

Table 13. Comparison of the coordination charges of atoms in crystals.

Metal	Compound	$Z^*_{X\text{-ray}}$	i, %	Z^*_{coord}
Cr	$CrSO_4 \cdot 7H_2O$	1.9	95	1.7
	$Cr(NO_3)_2 \cdot n\,H_2O$	1.2	68	1.1
	K_2CrO_4	0.1	29	0.3
Mn	$Mn(NO_3)_2 \cdot 4H_2O$	1.8	95	1.7
	$K_3Mn(CN)_6$	0.9	62	0.7
Fe	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	1.9	93	1.6
	$K_3Fe(CN)_6$	1.0	54	0.2
Co	$Co(NO_3)_3$	1.2	63	0.8
Os	$K_4Os(CN)_6$	1.5	59	−0.5
	OsO_3	0.8	44	0.6
	K_2OsCl_6	0.8	38	0.3
	K_2OsO_4	0.8	38	1.0
	K_2OsNCl_5	0.7	33	0.6
	$KOsO_3N$	1.0	25	1.2

It is evident from the data presented that, with the exception of osmium hexacyanide, the agreement between the calculated and experimental data may be regarded as good: the average discrepancy amounts to $0.3e$ or 5% of the ionic character. On the other hand, in $K_4Os(CN)_6$ there may be a trans-effect, unless one is dealing simply with an experimental error. In fact in the series of hexacyanides of manganese, iron, and osmium there is a systematic increase of the experimental charge on the central atom together with the increase of its electronegativity. If one remembers that the trans-effect should increase in the same series and that this gives rise to an increase in the ionic character of the central atom–ligand bond, one can understand why the charge of the metal atom increases despite the increase of its electronegativity.

The last method for estimating effective atomic charges in crystalline compounds is based on thermochemical data. By representing the energy of the bonds between atoms in the crystal as a sum of ionic and covalent terms, it is possible to estimate the ionic character of the bond, provided that the interatomic distances are known. The difficulty of this method consists in the fact that the covalent component of bond energy decreases with increasing ionic character according to a law which is, strictly speaking, unknown.

The effective atomic charges obtained by the energy method[113–116] are in good agreement with the values of Z^*_{intr} calculated from Eqn. (39). As an illustration, the "thermochemical" [116] values Z^*_{therm} and the theoretical values calculated for a single valence, i.e. the amount of ionic character of the bonds (i), are compared in Table 14. The average discrepancy amounts to $0.08e$ for each valence.

Thus, when account is taken of the structure of the crystals and ion–dipole interaction, the electronegativity method yields values for the ionic character of the bonds between atoms in crystalline compounds which differ from those determined experimentally by the Szigeti, X-ray spectroscopic, and thermochemical methods by amounts in the range 5–12%. Such precision is quite satisfactory for the majority of physicochemical problems.

Before concluding this Section, dealing with the determination of atomic charges, we shall consider briefly yet another parameter of the chemical bond, namely its multiplicity, which can be also calculated by the electronegativity method.

Table 14. Intrinsic charges of metal atoms determined from thermochemical data.

Crystal	Z_{therm}	i	Crystal	Z_{therm}	i	Crystal	Z_{therm}	i
NaF	0.97	0.89	MgO	0.74	0.75	Na_2S	0.62	0.73
NaCl	0.90	0.82	MgS	0.58	0.63	K_2S	0.65	0.75
NaBr	0.86	0.80	CaO	0.81	0.78	Cu_2S	0.54	0.56
NaI	0.82	0.77	SrO	0.80	0.78	MgF_2	0.89	0.82
KCl	0.98	0.84	ZnO	0.60	0.62	$MgCl_2$	0.70	0.67
KBr	0.96	0.81	ZnS	0.42	0.46	$MgBr_2$	0.70	0.67
KI	0.96	0.81	CdS	0.36	0.44	AlF_3	0.82	0.72
CuCl	0.45	0.64	MnS	0.44	0.50	$AlCl_3$	0.62	0.57
CuBr	0.42	0.60						

There exist two fundamental methods for the experimental determination of bond multiplicity—geometrical and spectroscopic. Both methods are based on a single principle—an increase in bond multiplicity increases its energy and leads to a corresponding decrease of the interatomic distance or an increase of the frequency of bond vibration. The first method was initially proposed by Pauling[68] and then developed by Hanic[16] and the second is due to Siebert[117]. However, in both these methods no account is taken of the effect of the ionic character of the bond on its energy and therefore they yield unambiguous results only for bonds of low polarity. It is of interest to develop an independent method for the determination of the multiplicity of bonds, including significantly polar bonds.

The simplest formulation of the concept of bond multiplicity N is

$$N = \frac{Z}{CN}. \qquad (40)$$

In coordination compounds or crystals $CN > Z$ and the interatomic space contains, apart from the electron cloud of the bond, also electrons withdrawn from the atoms as a result of ion–dipole interaction. Therefore the overall number of electrons per metal atom in coordination crystals is evidently

$$\Sigma = Z + (CN - Z) \cdot (1 - i_{el\text{-}stat}). \qquad (41)$$

Hence we obtain the following formula for the calculation of bond multiplicity in coordination crystals containing univalent anions:

$$N = \frac{\Sigma}{CN}. \qquad (42)$$

In polyvalent anions the overall number of electrons in the interatomic space is

$$\Sigma = Z_{cat.} + (CN \times Z_{an} - Z_{cat.})(1 - i_{el\text{-}stat}), \qquad (43)$$

and bond multiplicity can also be determined from Eqn. (42).

The results of the calculations by Eqns. (41) and (42) are compared in Table 15 with spectroscopic determinations of bond multiplicity in coordination crystals and complex ions.

The application of Eqn. (42) in the calculation of bond multiplicities in coordination crystals of the type AB leads to the following results:

for	$A^{I}B^{VII}N$	varies in the range	0.2—0.5
	$A^{II}B^{VI}$	» » »	0.4—0.7
	$A^{III}B^{V}$	» » »	0.6—0.8 .

It is clear from this equation that an increase in coordination number entails a decrease of N, which implies an increase in bond length. Since on going from a single to a double bond the length usually changes by 0.15–0.24 Å, it can be shown that the changes in N on going from CN = 4 to CN = 6 are consistent with the differences in interatomic distances usually observed in crystal chemistry.

Table 15. Bond multiplicities in hydrides and halides.

Compound	Ref.118	Ref.117	Ion	Ref.118	Ref.117
LiH	0.28	0.38	$(ZnCl_4)^{2-}$	0.61	0 75
NaH	0.27	0.27	$(ZnBr_4)^{2-}$	0.62	0.76
KH	0.26	0.26	$(CbCl_4)^{2-}$	0.62	0.70
CuH	0.42	0.68	$(CdBr_4)^{2-}$	0.62	0.86
BeH_2	0.60	0.69	$(CdI_4)^{2-}$	0.64	0.86
MgH_2	0.41	0.45	$(AlCl_4)^{-}$	0.80	0.99

The results obtained by Eqns. (43) and (42) are compared in Table 16 using oxygen-containing anions as an example. The agreement between the results of different methods can be regarded as satisfactory.

2. Physicochemical Properties and the Behaviour of Inorganic Substances

The knowledge of the ionic character of the bond is important for the understanding and theoretical calculation of many physicochemical properties of chemical compounds.

Table 16. Bond multiplicities in complex ions.

Ion	Ref.118	Ref.16	Ref.117	Ion	Ref.118	Ref.16	Ref.117
$(ClO_4)^{-}$	1.84	1.49	1.76*	$(PO_4)^{3-}$	1.45	1.41	1.41
$(SO_4)^{2-}$	1.66	1.53	1.53	$(AsO_4)^{3-}$	1.44	1.28	1.37
$(SeO_4)^{2-}$	1.65	1.45	1.52	$(VO_4)^{3-}$	1.44	1.37	1.49
$(CrO_4)^{2-}$	1.65	1.59	1.53	$(SiO_4)^{4-}$	1.25	1.21	1.19

* For Cl_2O_7.

Examples of the use of the concept of electronegativity for the calculation of interatomic distances and electronic polarisabilities of inorganic substances were given in the author's monograph[4]. In his paper Lakatos[119] quotes interesting examples of the solution of the converse problem. Without dwelling on these questions, which are quite fully described in the papers quoted and also in Ref. 97, we shall examine certain new aspects of the application of the concept of electronegativity in general chemistry.

The problem of the interpretation of the semiconductor properties of certain crystalline compounds was chosen as the first example. At the present time there exists no textbook on the chemistry of semiconductors in which the relation between the electronegativity and the width of the forbidden gap is not considered[120,121]. This is quite natural, since the transition of an electron from the valence band to the conduction band is inevitably associated with the nature of the chemical bonds and the mobility of electrons in the interatomic space, i.e., in other words, with the ionic and metallic character[122,123]. Bearing in mind that the energy of the forbidden gap itself is a consequence of the overall structure of the solid, its band structure, there is no point in seeking a relation between ΔE and ΔX only, which would undoubtedly be incapable of reflecting the entire set of specific features of the chemical compound. It is much more correct to introduce ΔX into an equation which already contains the ΔE values for the components of the compound determined for a purely covalent state (i.e. for the corresponding elements), so as to allow only for the deviation of the bond character in the given compound from the purely covalent state. The Schomaker–Stevenson equation[13] is a classical example of such an application of electronegativity:

$$r_{AB} = r_A + r_B - 0.09\Delta X_{AB} \quad . \qquad (5)$$

In complete agreement with this principle, the present author has proposed the following relation[124] between ΔE and ΔX:

$$\Delta E_{AB} = \Delta E_A + \Delta E_B + a\Delta X_{AB} - b\bar{n}_{AB} \qquad (44)$$

where ΔE_A and ΔE_B are the widths of the forbidden gap for the elements A and B (determined for the corresponding pure elements), $\bar{n}$ the average value of the principal quantum number, and a and b are constants. Tests of this equation using all the values of ΔE_{AB} known in 1964 showed that the average error is 0.2 eV. The equation of course constitutes the simplest method of taking into account the effects of the ionic and metallic character of the bond on the energy of the forbidden gap and requires further improvement, particularly as regards a more correct determination of the role of the metallic character of the bond. However, the principle of the derivation of the equation itself appears to be correct (see also Hooge[125]). Comparison of the electronegativities ΔX of atoms forming crystals having the same structure with their melting points reveals a distinct relation—the greater is the covalent character of the bond the lower is the melting point[126]. Table 17 presents several pairs of compounds with the same structures (coordination numbers) and similar interatomic distances, but which differ appreciably in their electronegativities. Geologists believe[127] that this relation is responsible for the magmatic crystallisation sequence and processes involving the substitution of cations in crystals. The explanation for this relation is that the energy of the Coulombic interactions is much higher than the energy of the covalent component of the bond, and therefore an increase of ΔX entails an increase in the total bond energy (for further details, see Ref. 4). This finding also plays an important role in the determination of the mode of double decomposition reactions which occur with formation of combinations of the most ionic and the most covalent compounds[128] (however, here one should recall that the electronegativity method can be applied directly only to purely molecular cases and account must be taken of the coordination number, etc., when crystals are considered).

The use of the concept of electronegativity to characterise the acid–base properties of chemical compounds has

proved extremely fruitful. On the basis of the Lewis–Brønsted theory, it is readily seen that an increase of the negative charge of the oxygen atom in an oxide will entail an increase in its basic properties. Therefore it is possible to establish a proportionality between ΔX and the acidity of the medium set up by the given combination of atoms. Such an approach is interesting because one need not consider the specific features of the medium and one can characterise objectively the acid–base properties of substances. Examination of the acid–base properties of silicates from the standpoint of the concept of electronegativity is also useful because classical chemical methods are inapplicable to this case[129]. A new finding is that in the usual substitution of the hydroxy-groups in aluminosilicates by fluorine atoms there is an increase in the acid character of the compound.

Table 17. Dependence of the melting point on bond type.

Crystal	Interatomic distance	CN	ΔX	M.p., °C	Crystal	Interatomic distance	CN	ΔX	M.p., °C
AgCl	2.77	6	1.2	455	CaF_2	2.36	8	3.0	1378
NaCl	2.81	6	2.2	800	CdO	2.35	6	1.8	1400
LiI	3 00	6	1.6	450	CaO	2.40	6	2.5	2570
NaBr	2.98	6	2.0	766	Al_2O_3	1.91	6	2.0	2050
$ZnCl_2$	2.60	6	1.5	365	MgO	2.10	6	2.3	2800
$MgCl_2$	2.63	6	1.9	712	SiSi	2.34	4	0	1420
CdF_2	2.34	8	2.3	1100	ZnS	2.35	4	1.0	1850

The electronegativity method makes it possible to understand and to predict the changes in the acid–base properties of organic compounds as a result of changes in their structure or on introduction into the molecular skeleton of definite substituents. The general principle which can be used here is that, in consequence of the higher electronegativity of the carbon combined with the hydroxyl, the oxygen atom of the OH group is forced to saturate the electron affinity on the side of the H atom to a greater extent, as a result of which the latter becomes more polar, i.e. acid. Hence, one may conclude that halogeno-substituted acids will be stronger than the normal acid and that the increase in acid strength will be greater the higher is the electronegativity of the halogen. However, it should be recalled that in comparisons of this kind one must of course select related molecules in which the same number of hydrogen atoms are replaced at the same carbon atom, because otherwise the structural effect may compete with the inductive effect[130]. Thus, the electronegativity method has recently been successful in the interpretation of the ionisation of fluoro-substituted organomercury compounds and the correlations proved to be so precise that it was possible to determine the group electronegativities from the pK data[131].

Since the dissociation of complex ions depends on the relation between the energy of the ligand–central atom bond and the ligand hydration energy, it is clear that the instability constants of complex compounds will be functionally related to the covalent character of the latter and hence to the electronegativities of the atoms. Such relations have been indeed established for numerous examples and have been used successfully in the chemistry of complex compounds (for further details, see Refs. 4 and 132). In general, according to Nyholm[133], the establishment of correlations between bond strengths and the electronegativity of the central atom is extremely promising for the chemistry of complex compounds. In this connection it is of interest to examine Chernyaev's trans-effect rule. The essence of the latter is that, when certain atoms and radicals interact with ligands located in the trans-position with respect to them, they ionise the latter and render them capable of more rapid (and sometimes actually ionic) substitution. A direct relation between the magnitude of the trans-effect and the covalent character of the bond between the given ligand and the central atom is a firmly established fact. It is quite clear that the ionisation of the species in the trans-position leads to a change in energy and in most cases to an increase in the strength of its bond, but the increased effective charge on the ligand results also in a sharp increase of its hydration energy, which facilitates the dissociation of this atom.

On the basis of what has been said above, the parallel variation of the position of the ligands in the trans-effect series and their electronegativities is evident[134] and it is clear why the same ligands, for example thiocyanato- and nitro-groups, can occupy different positions in the trans-effect series depending on the atom via which they are combined with the complex-forming metal.

The most interesting is the case of the combination of the central atom of the complex with a nitro-group and a chlorine atom. The electronegativity of both ligands is 3.2 and, other conditions being equal, their trans-activities should be the same. However, calculation of the effective coordination charge in complexes of di- or tetra-valent platinum by Eqn. (45) shows that in the first case $Z^*_{coord} < 0$ and in the second $Z^*_{coord} > 0$. Since in the N–O bond the positive pole is located at the nitrogen atom and the negative pole at the oxygen atom, it is easy to see that in complexes of divalent platinum with the NO_2 group the N–O bond length will be greater than in similar complexes of tetravalent platinum. These changes in bond length are consistent with the decrease in the multiplicity of the nitrogen–oxygen bond in platinum(II) complexes and its increase in platinum(IV) complexes relative to the normal state of the nitro-group. Since a decrease of the bond multiplicity of a given atom is accompanied by a decrease of its electronegativity on the opposite side, $X_{NO_2}(Pt^{II})$ will be less than X_{Cl} and $X_{NO_2}(Pt^{IV})$ will be greater than X_{Cl}. In accordance with what has been said above, this finding implies that the trans-effect of the nitro-group in platinum(II) compounds will be greater than the trans-effect of chlorine and that the converse relation will obtain in platinum(IV) compounds. It is known[135] that there is indeed a difference between the trans-effects of NO_2 and Cl but the postulated difference between the properties of the nitro-groups in complexes of di- and tetra-valent platinum still requires experimental tests[4,136].

Bearing in mind that in complexes of trivalent cobalt and gold with the nitro-group the central atoms have effective positive coordination charges, as can be readily seen from Tables 5 and 8 and Eqns. (39), the behaviour of the NO_2 group will be the same as in platinum(IV) complexes. On the other hand, in the nitrite complexes of trivalent metals of the platinum group the central atoms have an effective negative coordination charge and therefore the trans-effect of the NO_2 group will be greater than that of chlorine.

If these predictions prove to be valid and considerations based on charges do indeed play an important role in the determination of the trans-effect of the nitro-group, then one may postulate the possibility of a change in the trans-activity of NO_2 even for the same valence of the central atom, for example platinum. Thus in the iodide complexes of tetravalent platinum the nitro-group would exhibit a greater trans-effect than chlorine because here Z^*_{coord} is less than zero, while in fluorine-containing platinum(II) com-

plexes the relations between NO_2 and Cl may become the same as for tetravalent platinum because of the effective positive charge on the central atom of the complex. The variation of the trans-activity of ligands as a function of the composition of the complex can be regarded as a manifestation of the cis-effect in the inner sphere of complex compounds.

Of the entire wide variety of chemical properties and behaviour of simple inorganic compounds, we shall examine in this Section only one example each of the analysis and synthesis of substances, which can be interpreted or predicted from the standpoint of the concept of electronegativity.

The concept of electronegativity was recently successfully applied by Rozen and coworkers[137,138] in the problem of the separation of elements by extraction, or more precisely the problem of selecting optimum organic compounds for use as extractants. These workers showed that the electronegativities of the radicals are an important characteristic of compounds such as substituted tributyl phosphates and the analogous phosphonates. It is significant that the electronegativities found from the extraction of uranyl nitrate also describe satisfactorily the capacity of substances to be extracted by nitric acid, i.e. the relation obtained is of general importance. It has also been shown[138] that the Hammett–Taft equation can be derived from equations involving electronegativities. Therefore the latter can be used successfully also to describe the reactivities of organic compounds.

The findings arrived at with the aid of the electronegativity method proved fruitful also in the synthesis of new compounds. The synthesis of salts with mixed anions of the type MABC ... appears to be very promising, since by varying the anions A, B, and C, it is possible to increase almost without limit the range of chemical compounds of the given metal. Mixed salts are obtained by the combination of homogeneous salts, for example

$$PbF_2 + PbCl_2 = 3PbFCl\,, \qquad (45)$$

or by hydrolytic reactions, for example

$$MoCl_5 + H_2O = MoOCl_3 + 2\,HCl\,, \qquad (46)$$

or by double-decomposition reactions, for example

$$TiBr_4 + Cl_2O = TiOBr_2 + 2\,ClBr\,. \qquad (47)$$

However, it is difficult to expect the formation of substances in new valence states by these reactions. Therefore a very attractive procedure is the preparation of the mixed salts by reactions of the type

$$MA + B = MAB\,, \qquad (48)$$

where B is a halogen or a chalcogen, but there is then a possibility of displacement reactions if the oxidising capacity of the atom B is higher than that of the atom A.

Calculation of the effective coordination charges of variable-valence metals present in crystalline compounds in the lower-valence state showed that in most cases they are negative[4]. This can be understood when the coordination number of the metal is large, and the bonds which it forms with its nearest neighbours are significantly covalent; in other words, when the metal has given up fewer electrons for the formation of the bonds than the number it has received from them. Physically, a negative charge implies that the free electron pairs of the anions interact with the vacant sites of the cations. Finally, we must recall Z^*_{coord} is a concept reflecting the situation in the interatomic space and not within the atomic skeleton and this is in fact an important factor in oxidisation processes.

If we now return to Eqn. (48), we readily see that, when there is a negative charge on the atom M, the effect of the oxidant B should lead not to displacement of A but to an increase of the valence of M, i.e. the formation of a salt with mixed anions. Experiments confirmed this conclusion: with salts of copper, mercury, thallium, tin, chromium, manganese, and platinum, the present author succeeded in obtaining oxidised salts with mixed anions[139-149].

A few words must also be said about the change in the nature of the bond on heating and about the effects of such changes on chemical properties. It is clear from general considerations that the chemical bond can change as the molecule or crystal is heated. On heating, a solid melts and is then converted into a gas. Evidently, these processes are accompanied by a decrease of the ionic character of chemical bonds. One can also arrive at the conclusion that, within the same state of aggregation, heating increases the covalent character of the bond. In fact on heating the material expands due to the increased amplitude of atomic vibrations. The increase in volume may be interpreted in terms of the statistical decrease of the coordination number, which should entail a decrease of the ionic character of the bond. Physically, this has the following meaning: as the vibration amplitude increases, there is an increased frequency of instances when the oppositely charged ions approach one another to a distance so short that one can speak of the formation for a very brief instant of a molecule or molecular complex; the increase in the proportion of the molecular state in the crystal as the latter is heated is in fact consistent with the increased contribution of the covalent component to the chemical bonds of the substance.

The above considerations have found experimental justification. Thus Jones et al.[99] showed by Szigeti's method that, as alkali halide crystals are heated, their effective charges fall, i.e. there is an increase in the covalent component of the bond. Quantitatively this increase amounts on average to $0.02e$ per 100 deg.

Such increase in covalent character may give rise to significant changes in the distribution of the effective charges in the crystal. For example, when MnO is heated to 350°C, the ionic character of the bond decreases by $0.07e$ or from $0.71e$ (see Ref. 4, p. 173) to $0.64e$. Hence the effective coordination charge of the manganese atom in the MnO crystal changes from ± 0.26 to -0.16, i.e. there is a reversal of the sign of the charge. It is interesting that it is precisely at this temperature that the heating curve for MnO in air shows an exothermic maximum corresponding to the oxidation of manganous oxide to Mn_2O_3. This example illustrates the possibility of regarding oxidisation reactions which occur on heating from the standpoint of the system of the effective atomic charges in the substance and the effect of heating on the dynamics of this system. Knowing the ionic character of the bond in the initial state of the substance, it is possible to estimate the temperature ranges in which oxidation processes can begin.

The most pronounced changes in bond polarity are to be expected in coordination or dative bonds formed in the inner sphere of complex compounds, because the latter are formed by virtue of additional atomic orbitals and their energy frequently makes them less stable than the usual chemical bonds. This is why one may expect very considerable changes in chemical behaviour in complex compounds when the latter are heated even slightly.

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The above factual and theoretical data show that the concept of electronegativity can be successfully applied in the determination of atomic charges in molecules and crystals; at any rate, at the present time there is no other method for the determination of the ionic character of the bond as universal and simple as the electronegativity method. However, this method shows what the charge should be only if the latter is determined only by the normal valence bonds between atoms; when hydrogen bonds, trans-effects of atoms, or any other additional interaction is present, the atomic charges determined by the electronegativity method may differ from the actual values, but the difference itself can serve as a characteristic of the given type of interaction.

The formulae for and the magnitudes of the electronegativities of atoms permit the calculation of the fundamental properties of matter–bond energies and lengths, ionisation potentials, optical characteristics, and the distribution of electron density. This is why electronegativity will retain for a long time its importance in structural chemistry within the framework of the additive approach to the problems of molecular structure. Therefore, the present author believes that even the discovery of new properties and effects of the chemical bond will not entail the rejection of this concept.

The above view does not of course imply that the concept of electronegativity is free from disadvantages and that it is able to reflect all the features of the atomic and electronic structure of matter known at the present time. In this connection it is useful to consider briefly the controversy concerning the role and limits of applicability of the concept of electronegativity which occurred recently.

The concept of electronegativity, like other methods of theoretical chemistry, has its critics as well as supporters. The former can be divided into two groups—some workers criticise particular schemes for the calculation or application of electronegativity and propose new more successful ones (from their point of view); others see fundamental defects in the concept of electronegativity and suggest that it be completely excluded from the arsenal of theoretical chemistry. The first group is the most numerous and includes many investigators who have been fruitfully developing the concept of electronegativity, but their electronegativity values will not be considered here, particularly since later studies, which incorporate all the constructive postulates put forward in recent years, are quoted in the present review.

The first negative criticism of the concept of electronegativity was made in the paper by Fajans[140], who reviewed Pauling's book. Fajans noted that, by ascribing to each element of the Periodic System a constant electronegativity value, one cannot arrive even at a qualitatively correct understanding of chemical phenomena and the physical properties of substances. For example, in chloroacetylene the chlorine atom has a positive charge, in chloroethylene a zero charge, and in chloroethane a negative charge, while $X_{Cl} > X_C$. We now know that the electronegativity of the carbon atoms varies with the degree of hybridisation of its bonds and can assume values ranging from 2.0 to 3.3 (see Table 6). Comparison of these electronegativities of carbon with the constant electronegativity of chlorine shows that the sign of the charge on the chlorine atom should indeed change on going from chloroacetylene to chloroethane.

The second serious criticism of Pauling's concept was made by Hückel[151], who tested the principle of additivity in calculations of electronegativity and compared the amounts of ionic character calculated from the dipole moments of halogeno-hydrocarbons and interhalogen compounds. In the same paper Hückel formulated for the first time the question of the dimensions of electronegativity and expressed his perplexity concerning the physical significance of the dimension "(energy)$^{1/2}$". Without dwelling on the factual inaccuracies which were pointed out in the present author's review of Hückel's work[152], we may mention that his comparison of the dipole moments of various molecules with the aim of determining the ionic character of the bonds is without foundation, since, on changing the composition, the contributions of the various components of the dipole moment can also change. The large relative errors observed by Hückel in additive calculations involving electronegativity are purely an arithmetical effect, which arises when a constant absolute error (0.1 electronegativity unit) is compared with the small difference $\Delta X = 0.3–0.9$, and has almost no influence on the accuracy of the calculation of chemical bond energies.

The dimensions of the concept of electronegativity were discussed above, and, concerning Pauling's values of X, one can only add that Pauling himself calculated the ionic character of the bonds by Eqns. (24) or (25), which involve ΔX^2. The present author has already pointed out[152] that there is a definite analogy between ΔX and the wave function, bearing in mind that in the latter case it is precisely $|\psi|^2$ that is physically significant.

In the critical article of Lakatos[86] the arguments of Fajans and Hückel are quoted and it is emphasised that electronegativity is not a constant, since it must have a certain range of values depending on the valence state, the ionic character of the bond, hybridisation, etc. Lakatos also points out that the amounts of ionic character of bonds are determined from various atomic properties and therefore it is frequently difficult to make them consistent.

Iczkowski and Margrave[52] again draw attention to the differences in the dimensions of electronegativities determined by different methods and believe that the most correct representation of electronegativity is in the form of a potential. Together with Hückel, these authors believe that the main reason for the successful application of electronegativity in chemistry is that this quantity reflects the periodic variation of properties in Mendeleev's system.

In 1962 Syrkin[153] published a critical paper on the concept of electronegativity. Noting that in the early stage of development this concept constituted an advance, he now concluded that at the present time it can no longer be used for a satisfactory interpretation of experimental facts and even less so for their prediction. This paper is unfortunately not free from factual inaccuracies and Syrkin does not employ the most accurate system of electronegativities, as pointed out in the present author's review[154], but fundamentally his formulation of the problem is valid. The facts which have accumulated at the present time no longer fit within the Procrustean bed of constant electronegativities and require successive corrections for ionic character, multiplicity, and other characteristics of the chemical bond which are frequently unknown *a priori*. The question arises whether the numerous corrections and additions are justified by the results which can be gained with the aid of electronegativity. Syrkin gives a negative answer. The data presented above suggest that the answer is yes.

Finally in recent years Spiridonov and Tatevskii[155] published a series of papers in which they repeated the concrete objections of Hückel and Iczkowski but, in contrast to the other authors, they suggest a fundamental contradiction between the concept of electronegativity and quantum mechanics and therefore they reject the concept itself. They called for the application in chemistry of the rigorous methods of quantum mechanics. However, the trouble is

that such methods do not exist at the present time and it is not clear whether the many-electron problem can be solved rigorously, in principle, in a general form. For this reason, no one, including Spiridonov and Tatevskii, uses rigorous quantum-mechanical methods in their practical work. In reply to the criticism of these workers[156,157], a detailed analysis of their comments was made and it was shown on concrete examples that their wish for more rigorous solutions is at the present time unrealistic. The views of Spiridonov and Tatevskii are indirectly disproved by the use and development of the method of electronegativity by outstanding specialists in the field of quantum chemistry such as Pauling, Mulliken, Hinze and Jaffe, and finally Coulson[158].

Considering the criticism of the concept of electronegativity as a whole, we arrive at the paradoxical conclusion that here everyone is right—both the adherents and the opponents of the concept. The question is evidently what are the limits of applicability of this method. The present author has already stated earlier and believes it superfluous to repeat that, with the aid of electronegativity, one can determine directly the sign and magnitude of the charge only for atoms in molecules and crystals. In all remaining cases it is necessary to determine whether or not the given property depends on the polarity of the chemical bond and only if the answer is in the affirmative can one proceed to consider the concrete application of electronegativity values in familiar or newly derived equations.

The greatest defect of the concept of electronegativity is that the simplicity of the mathematical formulation led to the disappearance of the potential barrier which must be overcome by the investigator in order to master a given field and therefore the concepts and values of electronegativity are sometimes employed by incompetent persons. Incorrect application of the method merely brings it into disrepute.

Returning to the problems of the chemical bond, one would wish to mention in conclusion, a general characteristic of the modern state of this field of science. As our knowledge about the electronic structure of matter deepens, the theory of the chemical bond simultaneously develops, many simple physical characteristics and concepts become complex, and acquire a characteristic "structure". This was the case earlier with the dipole moment. A similar change is now taking place in the "chemical shift". Simple facts such as the shortening of the bond or the increase of the dissociation energy are in fact the result of at least two simultaneous trends, changes in the polarity and hybridisation of bonds, and this is why it is impossible to derive from such values unambiguous information about the nature of the chemical bond.

Precisely for this reason our concepts such as atomic radii, refractions, and electronegativities become complex and require that account be taken of the specific features of the environment of the given element. This is quite reasonable and one may hope that, as science progresses, the theoretical armoury of structural chemistry based on the principle of additivity will constitute an organic component of a more general and rigorous theory.

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Methods of Preparation and Chemical Properties of Aliphatic Halogeno-nitro-compounds

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The review deals with the literature on the nitrohalogenation of unsaturated compounds by addition to the latter of nitryl and nitrosyl halides and by the reaction of the unsaturated compounds with mixtures of nitrogen tetroxide and halogens. The condensation of nitro-alkanes with halogeno-carbonyl compounds, the nitration of halogeno-derivatives of aliphatic hydrocarbons, and the halogenation of nitro-compounds have also been described. Work on the reaction of polyhalogeno-alkanes with metal nitrites and the replacement of a carboxy-group by a halogen and a nitro-group have been reviewed. Dehydrohalogenation, dehalogenation, and also reactions involving the substitution of the halogen atoms have been examined in the analysis of the chemical properties of halogenonitro-compounds. The review also deals with work on the reactions of halogenonitro-compounds with participation of the nitro-group. A brief report is given on the applications of halogenonitro-compounds.

CONTENTS

I. Introduction 351
II. Methods of preparation of halogenonitro-compounds 352
1. Nitrohalogenation of unsaturated compounds 352
2. Condensation of nitro-alkanes with halogeno-carbonyl compounds 354
3. Nitration of halogeno-derivatives of aliphatic hydrocarbons 354
4. Halogenation of nitro-compounds 356
5. Substitution of a halogen for the hydroxyl in nitro-alcohols 356
6. Double decomposition of polyhalogeno-alkanes with metal nitrites 357
7. Replacement of a carboxy-group by a halogen atom or a nitro-group 357
8. Synthesis of γ-bromodinitro-compounds 357
9. Other methods 357
III. Chemical properties of halogenonitro-compounds 358
1. Reactions with participation of the halogen atom 358
2. Reactions with participation of the nitro-group 359
3. Other reactions 359
IV. Applications of halogenonitro-compounds 360

I. INTRODUCTION

Among aliphatic nitro-compounds considerable interest attaches to halogenonitro-compounds in which there are two or three reaction centres: the halogen atom, the nitro-group, and, for substances with a primary or a secondary nitro-group, two or one "mobile" hydrogen atom. The presence of several reaction centres permits a wide range of reactions with these compounds.

Despite their undoubted interest, the chemistry of halogenonitro-compounds has not been reviewed so far. The present review presents a compilation of data on the syn

thesis and chemical properties of halogenonitro-compounds excluding α-halogenonitro-compounds. The latter, containing a halogen and a nitro-group at the same carbon atom, constitute a fairly large group of substances, which differs sharply in methods of preparation and properties from halogenonitro-compounds in which the halogen and the nitro-group are attached to different carbon atoms[1].

II. METHODS OF PREPARATION OF HALOGENONITRO-COMPOUNDS

1. NITROHALOGENATION OF UNSATURATED COMPOUND

a. Addition of Nitryl Halides to Unsaturated Compounds

Nitrohalogenation with nitryl chloride and fluoride only has been described[2-15] and the possibility of the addition of nitryl fluoride has been demonstrated in only one study[16]:

$$CF_3-\underset{\displaystyle R}{\underset{|}{C}}=CF-OR' + FNO_2 \rightarrow \begin{matrix} CF_3 \\ \diagdown \\ R \end{matrix}\!\!>\!C(NO_2)-CF_2-OR' ,$$

where R = F or CF_3 and R′ = alkyl.

Many investigators are inclined to believe that nitryl chloride adds to unsaturated compounds by a free-radical mechanism, although it is also capable of heterolytic dissociation[3,12,14]:

$$NO_2^+ + Cl^- \rightleftarrows NO_2Cl \rightleftarrows NO_2^{\cdot} + Cl^{\cdot}$$
$$\downarrow\uparrow$$
$$NO_2^- + Cl^+ .$$

However, in weakly polar media nitryl chloride largely dissociates with formation of free radicals[12]. This can account for the finding that, in the chloronitro-compounds formed, the nitro-group is attached to the terminal carbon atom of the double bond regardless of the electronic properties of the substituents:

$$R-CH=CH_2 \xrightarrow{NO_2^{\cdot}} R-\dot{C}H-CH_2-CH_2NO_2$$
$$R-\dot{C}H-CH_2NO_2 \xrightarrow{NO_2Cl} R-CHCl-CH_2NO_2 + NO_2^{\cdot} ,$$

where R = alkyl, CH_3OCO, CN, COOH, $C\begin{matrix} O \\ \diagdown\!\!\diagup \\ Cl \end{matrix}$, or a halogen.

The primary attack by the chlorine atom leads to the formation of dichlorides. There exist contradictory data on the reaction of styrene with nitryl chloride[2,3]. Steinkopf and Kühnel[2] isolated 2-chloro-1-nitro-1-phenylethane as the reaction product, but later Goddard[3] repeated the reaction and obtained 1,2-dichlorophenylethane and β-nitrostyrene, the formation of which takes place, in his view, according to the mechanism

$$C_6H_5-CH=CH_2 \xrightarrow{NO_2Cl} [C_6H_5-CHCl-CH_2NO_2] \xrightarrow{-HCl} C_6H_5-CH=CHNO_2 .$$

The isolation in a number of cases of 2-chloro-nitrites and pseudonitrosites[5,9] is evidence that either nitryl chloride reacts partially by a heterolytic mechanism or the $NO_2^{\cdot}$ radical attacks the carbon atom with formation of the

$$-\underset{|}{\overset{|}{C}}-ONO \text{ bond.}$$

The addition of nitryl chloride to acetylenic hydrocarbons can serve as a convenient method for the synthesis of unsaturated halogenonitro-compounds[11,14,15]:

$$RC\equiv CR' + NO_2Cl \rightarrow RCCl=CNO_2R' ,$$

where R = C_2H_5, C_4H_9, C_6H_5, or Cl and R′ = C_2H_5, C_4H_9, C_6H_5, Cl, or H.

In addition to α-chloro-β-nitrostyrene, Freeman and Emmons[14] isolated $\alpha\alpha$-dichloroacetophenone from the products of the reaction of phenylacetylene and nitryl chloride and proposed a probable mechanism for its formation:

$$C_6H_5-C\equiv CH \xrightarrow{NO_2} C_6H_5-\dot{C}=CHNO_2 \xrightarrow{NO_2Cl} C_6H_5CCl=CHNO_2$$
$$C_6H_5-C\equiv CH \xrightarrow{NO_2Cl} C_6H_5-\dot{C}=CHCl \xrightarrow{NO_2^{\cdot}} C_6H_5-\underset{|}{\overset{ONO}{C}}=CHCl \xrightarrow{NO_2Cl}$$
$$\rightarrow \left[C_6H_5-\underset{|}{\overset{ONO}{\dot{C}}}-CHCl_2\right] \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CHCl_2 .$$

The reaction of nitryl chloride with diene hydrocarbons has been little investigated[4,17]. When nitryl chloride was allowed to react with divinyl, isoprene, piperylene, and chloroprene, the products of the 1,4-addition of NO_2Cl and the products of their isomerisation with migration of the double bond towards the nitro-group were obtained together with dichlorides.

b. Reaction of Nitrosyl Halides with Unsaturated Compounds

Nitrosyl chloride adds to ethylenic hydrocarbons in accordance with the Markovnikov rule[18-37]. The primary product of the addition reaction, an unstable monomeric nitrosochloro-derivative, can react further in three principal ways[29]: (1) it can condense to a relatively stable dimer; (2) it can be oxidised to chloronitro-compounds; (3) it can isomerise to the oxime of a chloro-aldehyde (or ketone):

$$\left[\begin{matrix} C-CH \\ Cl\ NO \end{matrix}\right]_2 \rightleftarrows \begin{matrix} C-CH \\ Cl\ NO \end{matrix} \rightarrow \begin{matrix} C-CH \\ Cl\ NO_2 \end{matrix}$$
$$\downarrow$$
$$\left[Cl-\underset{|}{\overset{|}{C}}-CH-N=\underset{\downarrow}{\overset{\downarrow}{N}}-CH-\underset{|}{\overset{|}{C}}-Cl\right] \qquad \begin{matrix} C-C=NOH \\ Cl \end{matrix} .$$
$$O\ O$$

The mode of reaction depends on the structure of the initial hydrocarbon and its chloronitroso-derivative. The second and third processes, oxidation and isomerisation, depend on the first—the capacity of the monomeric chloronitro-compounds to be converted into the dimer and on the stability of the dimeric form.

The presence of electron-acceptor atoms and groups at the carbon atom adjacent to the nitroso-group reduces the electron density of the –N=N– bond and favours the dissociation of the dimer into monomeric molecules, and, conversely, electron-donor substituents increase the stability of the dimer.

As a rule the reaction mixture contains products formed by all three reactions. However, depending on the structure of the initial olefin, one or other product predominates. The nature of the product depends on the relative rate of addition of nitrosyl chloride (NOCl) to the olefin and the oxidation of the product to a chloronitro-compound and a dichloro-derivative. If the oxidation is faster than the addition, the main reaction product is the chloronitro-compound. Thus, symmetrical and asymmetric alkylethylenes, and particularly polyalkylethylenes, yield mainly crystalline dimeric chloronitroso-derivatives and only small amounts of chloronitro-compounds. Trimethylethylene, isobutene[38,39], 2,2,3-trimethylbut-3-ene[29], 1-methylcyclohexene, 1-ethylcyclohexene, but-2-ene[30], pent-2-enyl-2-methylbut-1-ene, 2-(*p*-tolyl)propene[29], and

tetramethylethylene[40] react in this way. The chloronitro- and dichloro-compounds are the main products of the reaction of nitrosyl chloride with monosubstituted alkylethylenes—isopropylethylene[21], pent-1-ene, hex-1-ene, hept-1-ene, and 2,2-dimethylbut-3-ene[29]. If in an asymmetrically disubstituted ethylene one of the substituents has electron-acceptor properties, the chloro-derivative and the dichloro-compound predominate in the reaction products. This has been demonstrated for α-methylstyrene[41].

The addition of nitrosyl chloride takes place in accordance with the polarisation of the double bond. Allyl chloride, vinyl chloride, trichloroethylene[19], 2-chloropropene[33], methyl methacrylate, 3,3,3-trichloromethylpropene, 2-nitropropene[34], and methyl acrylate[35] react in this way.

The conversion of chloronitroso-compounds into chloronitro-compounds probably takes place via a stage involving the formation of diazo-nitrates, for example[29]:

$$CH_3{-}CX{=}CH_2 \xrightarrow{NOCl} CH_3CX(NO){-}CH_2Cl \xrightarrow{2NOCl} CH_3{-}CX(N_2ONO_2){-}CH_2Cl + 2Cl;$$

$$CH_3{-}CX(N_2ONO_2){-}CH_2Cl \xrightarrow{NOCl} CH_3{-}CXCl{-}CH_2Cl + N_2 + 2NO_2;$$

$$CH_3{-}CX{=}CH_2 + NO_2^{\cdot} \rightarrow CH_3{-}\dot{C}X{-}CH_2NO_2 \xrightarrow{NOCl(Cl)} CH_3{-}CXCl{-}CH_2NO_2;$$

where X = Cl, $COOCH_3$, NO_2, or CCl_3.

When 2,2-dimethylpent-3-ene reacts with nitrosyl chloride, a mixture of chloronitro-products is formed[31]:

$$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH{=}CH{-}CH_3 + NOCl \rightarrow \begin{cases} (CH_3)_3C{-}CHNO_2{-}CHCl{-}CH_3 \\ (CH_3)_3C{-}CHCl{-}CHNO_2{-}CH_3 \end{cases}.$$

Nitrosyl chloride reacts with tetrafluoroethylene, chlorotrifluoroethylene, and the asymmetric dichlorodifluoroethylene with formation of nitro-compounds when the mixture is passed through a heated glass tube[25]:

	Yield
$CF_2{=}CF_2 \xrightarrow[NOCl]{50^\circ} CF_2ClCF_2NO_2$,	63%
$CF_2{=}CFCl \xrightarrow[NOCl]{100^\circ} CF_2ClCFClNO_2$,	67%
$CF_2{=}CCl_2 \xrightarrow[NOCl]{100^\circ} CF_2ClCCl_2NO_2$.	57%

The same products are formed when the reaction is carried out in a sealed tube[18,23] or in an autoclave at room temperature[26].

When nitrosyl chloride, tetrafluoroethylene, and chlorotrifluoroethylene were passed through a tube over ferric chloride at 45°C, nitroso-compounds, dichloro-compounds, chloronitro-compounds, and dinitro-compounds were isolated[37]. Similar results were obtained when nitric oxide (NO) was used instead of nitrosyl chloride[32,42]. Probably in this case the first reaction stage is the formation of nitrosyl chloride from nitric oxide and ferric chloride.

The addition of nitrosyl bromide and fluoride to unsaturated compounds has been investigated to a lesser extent. Only one reaction of nitrosyl bromide is known[24-26]:

$$CF_2{=}CF_2 + NOBr \rightarrow CF_2NO_2CF_2Br.$$

Tetra- and tri-fluoroethylene, and vinylidene fluoride readily react with nitrosyl fluoride, but nitro-compounds were not found among the products. Perfluoropropene reacts with nitrosyl fluoride only at 150°C. In the presence of calcium sulphate as the catalyst the yield of nitroalkanes is slight and without catalyst radical nitration products are formed exclusively[43].

Degradation products were obtained from perfluorobut-2-ene and nitrosyl fluoride at 200°C: $CF_3CF_2NO_2$, CF_3NO_2, etc.[44]

Depending on the molar ratio of the reactants, diene hydrocarbons combine with one or two molecules of nitrosyl chloride[22]. Thus diallyl reacts with nitrosyl chloride to form 5-chloro-6-nitrohexene, 2,5-dichloro-1,6-dinitrohexane, and also 5,6-dichlorohex-1-ene and 1,2,5,6-tetrachlorohexane, i.e. the double bonds react completely independently of one another and the addition of nitrosyl chloride takes place as with monosubstituted olefins. Butadiene behaves similarly:

$$CH_2{=}CH{-}CH{=}CH_2 \rightarrow \begin{cases} \xrightarrow{+NOCl} CH_2{=}CH{-}CHCl{-}CH_2NO_2 \\ \xrightarrow{+2\,NOCl} CH_2NO_2{-}CHCl{-}CHCl{-}CH_2NO_2 \end{cases}.$$

Nitrochlorination of acetylene derivatives with nitrosyl chloride permits the synthesis of a wide variety of 1,2-chloronitro-alkenes in a single stage:

$$RC{\equiv}CR' \xrightarrow{NOCl} \underset{\displaystyle Cl\ \ NO}{RC{=}CR'} \xrightarrow{O} \underset{\displaystyle R\ \ R'}{ClC{=}CNO_2}.$$

Perrot and Berger[27] obtained α-chloro-β-nitrostyrene and its derivatives from phenylacetylene and nitrosyl chloride:

$$RC_6H_4C{\equiv}CH + NOCl \rightarrow RC_6H_4C(Cl){=}CHNO_2,$$

where R = H, p-CH_3, o- and p-Cl, or m-NO_2 and p-NO_2.

c. Nitrohalogenation of Saturated Compounds by Nitrogen Tetroxide–Halogen Mixtures

The structure of the products of the nitrohalogenation of olefins by N_2O_4–X_2 (X = Cl, Br, or I) in many ways depends on the reaction conditions, the structure of the initial olefin, and the nature of the halogen[45-52]. When the reaction is carried out in the vapour phase, free-radical processes predominate[47,53], since under these conditions N_2O_4 and X_2 dissociate into radicals: $N_2O_4 \rightleftharpoons 2NO_2^{\cdot}$, $X_2 \rightleftharpoons X^{\cdot} + X^{\cdot}$. The radical initiating the reaction can be either $NO_2^{\cdot}$ or $X^{\cdot}$ (the capacity for this decreases in the series Cl → Br → I). In the chloronitration of propene and butene at 260–275°C, the products are 1-chloro-2-nitro-alkanes[52] (the chlorine atom is more reactive):

$$R{-}CH{=}CH_2 + Cl^{\cdot} \rightarrow R\dot{C}HCH_2Cl,$$

$$R{-}\dot{C}HCH_2Cl + NO_2^{\cdot} \rightarrow RCHNO_2CH_2Cl,$$

$$R{-}\dot{C}HCH_2Cl + Cl_2 \rightarrow RCHClCH_2Cl + Cl^{\cdot}.$$

Vinyl chloride and bromide react with N_2O_4–Cl_2 and N_2O_4–Br_2 mixtures in different ways when the reaction temperature is raised from 250° to 325°C:[47]

$$CH_2{=}CHR + NO_2^{\cdot} \xrightarrow{255^\circ} CH_2NO_2\dot{C}HR$$

$$CH_2NO_2\dot{C}HR + X_2 \rightarrow CH_2NO_2CHRX$$

$$CH_2{=}CHR + X^{\cdot} \xrightarrow{325^\circ} CH_2X{-}\dot{C}HR$$

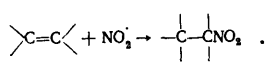
$$CH_2X{-}\dot{C}HR + NO_2^{\cdot} \rightarrow CH_2X{-}CHRNO_2$$

where R = Cl, Br. The different reactions can be accounted for by a change in the reactivity of the $NO_2^{\cdot}$ and $X^{\cdot}$ radicals with increasing temperature.

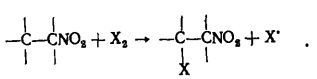
Sometimes a change in the relative proportions of the reactants (the olefin and the N_2O_4–X_2 mixture) leads to a change in the mode of addition[48]:

$$CH_2{=}CHCl \xrightarrow{N_2O_4+Br_2} \begin{cases} \rightarrow CH_2BrCHClNO_2 \\ \rightarrow CHClBrCH_2NO_2 \end{cases}.$$

Liquid-phase nitrohalogenation of unsaturated compounds takes place as a rule by a radical mechanism[45-50]. The reaction is then initiated by the $NO_2^{\cdot}$ radical:



The nitroalkyl radical formed is "captured" by the halogen:



For example,

$$CH_3{-}CH{=}CH_2 + N_2O_4 + I_2 \rightarrow CH_3{-}CHI{-}CH_2NO_2 ,$$
$$CH_3COO{-}CH{=}CH_2 + N_2O_4 + I_2 \rightarrow CH_3COOCHI{-}CH_2NO_2 ,$$
$$C_6H_5{-}CH{=}CH_2 + N_2O_4 + I_2 \rightarrow C_6H_5{-}CHI{-}CH_2NO_2 .$$

The free-radical mechanism explains particularly satisfactorily the reactions of fluoro-olefins with a mixture of N_2O_4 and I_2:[48,49]

$$N_2O_4 \rightarrow 2NO_2^{\cdot} ,$$
$$CF_2{=}CHX + NO_2^{\cdot} \rightarrow NO_2CHX\dot{C}F_2 + O_2NCF_2\dot{C}HX$$
$$\downarrow I_2 \qquad\qquad \downarrow I_2$$
$$O_2NCHXCF_2I + I^{\cdot} \quad O_2NCF_2CHXI + I^{\cdot} ,$$
$$CHX{=}CF_2 + ONO^{\cdot} \rightarrow CHX{-}CF_2ONO \xrightarrow{I_2} ICHX{-}CF_2ONO \rightarrow ICHX{-}COOH ,$$

where X = H, F, or perfluoroalkyl.

Bachman and Logan[51] carried out the reaction of ethylene, propene, and butenes with N_2O_4–I_2 and N_2O_4–Br_2 mixtures in the presence of an excess of nitrogen tetroxide and and isolated halogeno-nitrates, the formation of which they believe to be due to an ionic mechanism:

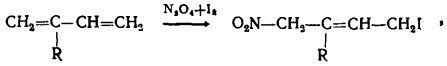
$$R{-}CH{=}CH_2 + Br_2 \rightarrow R{-}\overset{+}{C}H{-}CH_2Br + Br^- ,$$
$$R{-}\overset{+}{C}H{-}CH_2Br + N_2O_4 \rightarrow R{-}CHONO_2CH_2Br + NO^+ .$$

Stevens and Emmons[45] explain this finding by the presence of a large excess of nitrogen tetroxide in the reaction.

Diene hydrocarbons react with the N_2O_4–I_2 mixture by a 1,4-addition mechanism[46]:

$$CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_2NO_2{-}CH{=}CH{-}CH_2I .$$

With substituted butadienes, the attack by NO_2 radicals is directed preferentially to carbon atoms most highly enriched in electrons:



where R = CH_3 or Cl.

2. CONDENSATION OF NITROALKANES WITH HALOGENO-CARBONYL COMPOUNDS

The condensation of nitro-alkanes with halogeno-carbonyl compounds has been investigated relatively little[54-73]. It was first studied by Henry[54], who allowed chloral hydrate to react with nitromethane in the presence of potassium carbonate[54]:

$$CCl_3CH(OH)_2 + CH_3NO_2 \rightarrow Cl_3CCH(OH)CH_2NO_2 .$$

Later it was repeated[55,57,63,67,73] and extended to chloral homologues (butylchloral and bromal[63]) and other nitro-alkanes (nitroethane, phenylnitromethane[56], and 1-nitro-propane[55]).

The condensation of chloral hydrate with nitromethane takes place with an almost quantitative yield but the reaction is somewhat less complete with other nitro-alkanes. When the reaction was carried out in the vapour phase, contrary results were obtained—a better yield with nitro-butane[58].

The condensation of mono- and dichloroacetaldehyde and bromoacetaldehyde takes place with greater difficulty[59-62]. Fluoro-substituted aldehydes also enter into the condensation reaction with nitro-alkanes in the presence of alkaline catalysts[59-66,68,69]:

$$RCF_2CH(OH)_2 + R'CH_2NO_2 \rightarrow RCF_2CH(OH)CH(NO_2)R' ,$$

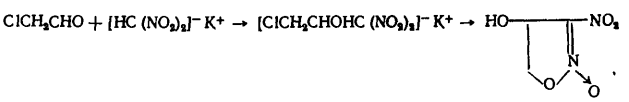
where R = F or C_2F_5 and R′ = H, CH_3, or C_2H_5.

Of the halogeno-substituted ketones, only 1,1,1-trifluoroacetone[68], 1,1,1-trifluorobutan-2-one[66], and perfluoroacetone[70] have been investigated in the condensation with nitro-alkanes:

$$CF_3COR + CH_3NO_2 \rightarrow CF_3CR(OH)CH_2NO_2$$

where R = CH_3, C_2H_5, or CF_3.

When the potassium salt of dinitromethane is condensed with chloroacetaldehyde hydrate, the product of the spontaneous cyclisation, 4-hydroxy-3-nitroisoxazoline *N*-oxide, was obtained instead of the expected potassium salt of γ-chloro-β-hydroxydinitropropane:[72]



3. NITRATION OF HALOGENO-DERIVATIVES OF ALIPHATIC HYDROCARBONS

a. Nitration with Nitrogen Oxides

When nitric oxide acts on chlorotrifluoroethylene and hexafluoropropane, nitro-derivatives are obtained in small amounts[42]:

$O_2NCF_2CFClNO$, $O_2NCF_2CFCl_2$, $O_2NCF_2CFClNO_2$, $CF_3CF(NO){-}CF_2NO_2$ и $CF_3CF(NO_2)CF_2NO_2$.

The addition of nitrogen dioxide to halogeno-olefins takes place by a free-radical mechanism with formation of dinitro-derivatives of halogeno-alkanes. This has been shown by numerous studies on the addition of nitrogen tetroxide to tribromoethylene[64], tetrachloro- and tetrabromoethylenes[65], tetrafluoroethylene[64,66-70], chlorotrifluoroethylene[24,66,71], and hexafluoropropene[69]. Together with halogenonitro-alkanes, the formation of halogenonitronitrites has been observed; on subsequent hydrolysis, the latter yield halogeno-substituted nitro-alcohols[74-87], nitrocarboxylic acids[78-80], or nitro-ketones[81].

In some cases the nitro-alcohol is formed preferentially[82-84]:

$$CH_2Cl{-}CH{=}CH_2 + N_2O_4 \rightarrow CH_2Cl{-}CH(OH){-}CH_2NO_2 ,$$
$$CH_2{=}\underset{\displaystyle CH_2Cl}{\underset{|}{C}}{-}CH_3 + N_2O_4 \rightarrow O_2NCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}(CH_3)OH$$

By allowing the complex $BF_3.N_2O_4$ to react with vinyl chloride at 0°C in chloroform, Bachman and Vogt[85] obtained 2,2-dichloronitroethane:

$$CH_2{=}CHCl + BF_3{\cdot}N_2O_4 \rightarrow Cl_2CHCH_2NO_2 .$$

They explained the formation of this product by the oxidative degradation of part of the vinyl chloride.

The nitration of perfluorobutadiene with N_2O_4 yields 1,4-dinitroperfluorobut-2-ene and 1-nitroperfluorobut-2-enyl nitrite[86]:

$$CF_2=CF-CF=CF_2 \longrightarrow O_2N-CF_2-CF=CF-CF_2-NO_2 \quad O_2N-CF_2-CF=CF-CF_2-ONO$$

On hydrolysis the nitrite is converted into γ-nitroperfluorobutyric acid and on treatment with alcohols or on ammonolysis it yields the esters of this acid or the amide.

Under the action of nitrogen oxides, halogenoacetylenes are converted into halogenonitro- and halogenodinitroethylenes[87-89]:

$$IC\equiv CI + N_2O_4 \rightarrow IC(NO_2)=C(NO_2)I,$$
$$IC\equiv CI + N_2O_3 \rightarrow I_2C=C(I)NO_2,$$
$$ClC\equiv CCl + N_2O_4 \xrightarrow{(C_2H_5)_2O} ClCH=C(Cl)NO_2.$$

Products of the substitution of halogen and hydrogen atoms were obtained in the nitration with N_2O_4 of 2,3-dibromopropene[90] and dichloroethylene[91] respectively:

$$CH_2=C(Br)-CH_2Br \rightarrow CH_2=C(Br)-CH_2NO_2$$
$$(CHCl)_2 \rightarrow NO_2CCl=CHCl.$$

b. Nitration of Halogeno-Alkenes and Halogeno-Alkanes with Nitric and Other Acids

The nitration of halogeno-alkenes with nitric acid or its mixtures with other acids takes place by an ionic mechanism and leads to the formation of products resulting both from the addition of the NO_2 group and the substitution of hydrogen or halogen atoms. In the latter case halogenonitro-alkenes are formed. The nitration process is complicated by side reactions involving oxidation. When a mixture of concentrated nitric and sulphuric acids reacts with tetrachloroethylene, tetrachloro-1,2-dinitroethane is formed[92]:

$$Cl_2C=CCl_2 + HNO_3 \xrightarrow[H_2SO_4]{} O_2NCCl_2CCl_2NO_2.$$

By nitrating 1,1,5-trichloropent-1-ene or 1,1-dichloropent-1-ene with nitric acid, Zakharkin[10] obtained both mono- and di-nitro-derivatives:

$$Cl_2C=CHCH_2CH_2CH_2Cl + HNO_3 \rightarrow Cl_2CCH(NO_2)CH_2CH_2CH_2Cl + Cl_2C(NO_2)CH(NO_2)CH_2CH_2CH_2Cl,$$
$$Cl_2C=CHC_3H_7 + HNO_3 \rightarrow Cl_2CCH(NO_2)C_3H_7 + Cl_2C(NO_2)CH(NO_2)C_3H_7$$

He believes that the formation of 1,1,1-trichloro-2-nitroalkanes can be explained by the reaction of hydrochloric acid (formed in the oxidation of the $Cl_2C=CH$ group) with nitric acid ($HNO_3 + HCl \rightarrow NOCl + Cl_2 + H_2O$)—the addition of nitrosyl chloride and the oxidation of the resulting products; the formation of nitryl chloride by the reaction of hydrochloric and nitric acids and its subsequent addition to the double bond cannot be excluded.

On being refluxed with an excess of nitric acid, dichloroethylene is converted into trichloronitroethylene in a good yield[93]. Under the action of fuming nitric acid or its mixtures with sulphuric acid, tetraiodoethylene yields 1,2,2-tri-iodonitroethylene[87].

Kooijman and Overhoff[94] nitrated chloro-olefins with nitric acid in such a way that the double bond in the initial olefins was not affected:

$$CH_2=C(CH_3)CH_2Cl + HNO_3 \rightarrow O_2NCH=C(CH_3)CH_2Cl.$$

A method of nitration of olefins with a mixture of sodium nitrite and dilute sulphuric acid has been patented[95,96]:

$$CH_2=C(CRR^1X)-CHR^2R^3 + NaNO_2 \xrightarrow{H_2SO_4} CH_2=C(CRR^1X)-CR^2R^3NO_2,$$

where R, R^1, R^2, and R^3 = H or alkyl and X = halogen.

The reaction of 2,3-dibromopropene with nitric acid in dichloroethane at 40–50°C yields a mixture of these products[97]:

$$BrCH_2C(Br)=CH_2 + HNO_3 \rightarrow (NO_2)_2CCH_2Br + (NO_2)_2CHCH_2Br + BrCH_2-C(NO_2)(Br)-COOH.$$

Martynov and coworkers[98-102] obtained the products of the oxidation of halogeno-olefins with the nitrating mixture. They isolated halogenonitro-acids and their chlorides.

Nitrofluorination of olefins and their halogeno-derivatives with a mixture of nitric acid and anhydrous hydrogen fluoride can serve as one of the methods of preparation of fluoronitro-alkanes:

$$HF + HNO_3 \rightleftarrows O_2N^+ + 2F^- + H_3O^+$$
$$>C=C< + O_2N^+ \rightarrow \left[>C(NO_2)-\overset{+}{C}<\right] F^- \rightarrow >C(NO_2)-C(F)<.$$

This reaction was achieved for the first time with tetrafluoroethylene[103]:

$$CF_2=CF_2 + HNO_3 + HF \rightarrow CF_3CF_2NO_2.$$

The study of the nitrofluorination of asymmetric halogeno-olefins showed that the mode of addition is determined by the polarity of the double bond[103-106]:

$$CHCl=CH_2 \xrightarrow{HF+HNO_3} CHFCl-CH_2NO_2,$$
$$CF_2=CFCF_3 \xrightarrow{HNO_3+HF} (CF_3)_2CFNO_2,$$
$$CH_2=CHCOOCH_3 \xrightarrow{HF+HNO_3} CH_2F-CH(NO_2)COOCH_3 + CH_2OH-CHNO_2-COOCH_3.$$

The nitration of saturated hydrocarbons and their derivatives was first investigated by Konovalov. By heating a mixture of dilute nitric acid with 1-chloro-2-methylpropane or 1-chloro-3-methylbutane in sealed tubes, he obtained the corresponding mononitro-derivatives, the nitro-group substituting the hydrogen at the tertiary carbon atom[107,108]:

$$(CH_3)_2CH(CH_2)_nCl + HNO_3 \rightarrow (CH_3)_2C(NO_2)(CH_2)_nCl,$$

where n = 1, 2.

Shechter and Conrad[109] achieved the vapour-phase nitration of 1,1,1-trifluoropropane at 437–462°C in the presence of oxygen and isolated 3,3,3-trifluoro-1-nitropropane. When the reaction was carried out at 395°C, a mixture of 3,3,3-trifluoro-1-nitropropane and 2,2,2-trifluoronitroethane was isolated in proportions of 3 : 2.[110]

Chloronitro-alkanes have been obtained by the action of a mixture of sulphuric acid and ammonium nitrate on the corresponding chloro-alkanes[111]:

$$RCH(Cl)CH_3 \xrightarrow[H_2SO_4]{NH_4NO_3} RCH(Cl)CH_2NO_2,$$

where R = CH_3 or C_2H_5.

4. HALOGENATION OF NITRO-COMPOUNDS

a. Halogenation of Nitro-Olefins

Unsaturated nitro-compounds (in solution) combine with chlorine or bromine at the double bonds in the cold or on heating, with formation of dihalogeno-derivatives[112-117]. The reaction involves a heterolytic mechanism:

$$RCH{=}C(NO_2)R' + X_2 \rightarrow RCH(X)C(X)(NO_2)R' .$$

When two electronegative substituents are present at the double bond, more severe conditions are required for the addition of the halogen. Thus chlorine adds to vicinal dinitro-olefins after the olefin has remained in contact for a long time with liquid chlorine in sunlight[115].

The double bond conjugated with the nitro-group in 1-nitrobutadiene[114] is deactivated and, when bromine reacts with 1-nitrobutadiene between −10° and 18°C, only one molecule of bromine adds to the olefin with formation of the dibromo-derivative in 99% yield:

$$NO_2CH{=}CH{-}CH{=}CH_2 + Br_2 \rightarrow NO_2CH{=}CHCHBrCH_2Br .$$

Since the nitro-group is a powerful electron acceptor, the electrophilic addition of bromine to β-nitrostyrene is difficult and therefore for this reaction to take place, the reaction mixture must be heated in chloroform[116].

b. Halogenation of Nitro-Alkanes

Riley and McBee[118,119] showed that the chlorination of nitro-alkanes in the absence of bases leads to the formation of β-chloronitro-alkanes. Bromination in the absence of base yields the same products as in the presence of bases, i.e. α-bromonitro-compounds are produced. The authors believe that substances such as phosphorus pentoxide favour the formation of the β-isomer by displacing the equilibrium of the reaction

$$RCH_2NO_2 \rightleftarrows RCH{=}N\begin{matrix}O\\ \diagup\\ \diagdown\\ OH\end{matrix} .$$

Riley and McBee explained the difference in the behaviour of chlorine and bromine by the fact that chlorine reacts very fast and the concentration of the nitronic acid is negligible, while bromination takes place slowly, and the conversion of the nitro-alkane into the aci-form takes place much more rapidly and therefore there is sufficient time for the aci-form to react with bromine with formation of α-bromonitro-alkane.

Sayles and Degering[120] described the chlorination of nitrobutane on irradiation with ultraviolet light in the presence of phosphorus pentoxide, the sole product according to their data being 4-chloro-1-nitrobutane:

$$CH_3CH_2CH_2CH_2NO_2 + Cl_2 \xrightarrow{P_2O_5} ClCH_2CH_2CH_2CH_2NO_2 .$$

However, in the chlorination of nitrobutane under analogous conditions Erm[121] obtained in addition 3-chloro-1-nitrobutane. He believes that the mode of reaction depends mainly on the intensity of the ultraviolet irradiation.

5. SUBSTITUTION OF A HALOGEN FOR THE HYDROXYL IN NITRO-ALCOHOLS

As in simple aliphatic alcohols, the hydroxy-group of nitro-alcohols can be replaced by a halogen when the latter reacts with the halides of phosphorus and sulphur acids[122-148]. This reaction is used to demonstrate the presence of the hydroxy-group in nitro-alcohols and for the preparation of halogenonitro-alkyls with a definite structure.

The substitution of the hydroxy-group of nitro-alcohols by a chlorine atom was first achieved by Henry[54,122-125], who treated the nitro-alcohols with phosphorus pentachloride:

$$RCH(NO_2)CH_2OH + PCl_5 \xrightarrow{K_2CO_3} RCH(NO_2)CH_2Cl ,$$

where R = H or CH_3, and

$$RCH(OH)CH_2NO_2 + PCl_5 \xrightarrow{K_2CO_3} RCHClCH_2NO_2 ,$$

where R = CH_3 or CCl_3. Other β-chloronitro-alkanes were prepared similarly[126-130].

The substitution of the hydroxy-groups in nitro-diols by halogens under the action of phosphorus pentachloride takes place with much greater difficulty[131,137], while with trihydric alcohols a mixture of chloro-derivatives of various degrees of substitution and of phosphoric acid esters of the nitro-alcohols is produced[133]. Kleinfeller[133] synthesised tri(bromomethyl)nitromethane by the bromination of nitroisobutylglycerol with elemental bromine in the presence of red phosphorus[133]. The nature of the side products formed in this process was similar to that in the chlorination reaction.

A more convenient method for the substitution of the hydroxy-group by a chlorine atom consists in the treatment of nitro-alcohols with thionyl chloride in the presence of pyridine. The following chloronitro-compounds have been obtained by this procedure: $ClCH_2CH_2NO_2$, $O_2NCH_2CHClCH_3$, $C_2H_5CH(NO_2)CH_2Cl$;[132] $CH_3C(Cl)(NO_2)CH_2Cl$, $O_2N(C_2H_5)C(CH_2Cl)_2$;[138] $O_2NC(CH_2Cl)_3$;[139] $CH_3C(NO_2)_2CH_2Cl$, $ClCH_2C(NO_2)_2CH_2Cl$;[148] $CH_2NO_2CHClCH_3$;[146] $(O_2N)_3CCH_2Cl$.[147]

In the study of the reaction of thionyl chloride with nitrodiols in the presence of pyridine, Novikov and coworkers[140] concluded that the chlorinating agent is a complex of thionyl chloride with pyridine, formed relatively slowly. Therefore, on rapid addition of $SOCl_2$ to the mixture of the diol and pyridine, there is not sufficient time for the formation of the complex and the reaction can lead to the formation of cyclic sulphites[133].

Halogenonitro-alkanes can be prepared from the acetals of nitro-alcohols by treating the latter with phosphorus pentachloride[141]:

$$RR^1C(NO_2)CHR^2OCHOR^3 \xrightarrow{PCl_5} RR^1C(NO_2)CH(R^2)Cl ,$$
$$\quad\quad\quad

6. DOUBLE DECOMPOSITION OF POLYHALOGENO-ALKENES WITH METAL NITRITES

Henry[54,149] achieved the synthesis of 2-chloronitroethane and 3-chloro-1-nitropropane by the reaction of silver nitrite with the corresponding $\alpha\omega$-chloroiodo-alkanes:

$$Cl(CH_2)_nI + AgNO_2 \rightarrow Cl(CH_2)_nNO_2,$$

where $n = 2$ or 3. A number of $\alpha\omega$-fluoronitro-alkanes have been synthesised by the reaction of the corresponding $\alpha\omega$-bromofluoro- or $\alpha\omega$-fluoroiodo-alkanes with silver nitrite[150]:

$$F(CH_2)_nX + AgNO_2 \rightarrow F(CH_2)_nNO_2,$$

where X = Br or I and $n = 3$, 4, 5, or 6.

Halogenonitro-alkanes can be obtained also from di-halogeno-derivatives in which both halogen atoms are identical. Thus Work carried out the reaction of silver nitrite with 1,5-dibromopentane[151] and 1,5-dibromo-3-propylpentane[152] at room temperature and obtained the corresponding $\alpha\omega$-bromonitro-alkanes:

$$RCH(CH_2CH_2Br)_2 + AgNO_2 \rightarrow NO_2CH_2CH_2CH(R)CH_2CH_2Br,$$

where R = H or C_3H_7. 2-Bromo-3-nitropropene was obtained similarly from 2,3-dibromopropene[90].

Freidlina et al.[153] obtained 1,1-dichloro-3-nitropropene from 1,1,3-trichloropropene and silver nitrite using the different reactivities of the chlorine atoms:

$$ClCH_2CH{=}CCl_2 + AgNO_2 \rightarrow NO_2CH_2CH{=}CCl_2.$$

A method for the preparation of halogeno nitro-compounds by the reaction of polyhalogeno-compounds with alkali or alkaline earth metal nitrites in aqueous ethanol was patented in 1944:[154]

$$ClCH_2CH_2Cl + MNO_2 \rightarrow O_2NCH_2CH_2Cl$$

$$ClCH_2{-}\underset{OH}{CH}{-}CH_2Cl + MNO_2 \rightarrow O_2NCH_2\underset{OH}{CH}{-}CH_2Cl.$$

7. REPLACEMENT OF A CARBOXY-GROUP BY A HALOGEN ATOM OR A NITRO-GROUP

Silver salts of *gem*-dinitro-carboxylic acids are converted into bromonitro-alkanes under the action of elemental bromine[155-157]. 4-bromo-2,2-dinitrobutane and 1,5-dibromo-3,3-dinitropentane have been obtained in this way:

$$CH_3\overset{NO_2}{\overset{|}{C}}(NO_2)-CH_2CH_2-COOAg \xrightarrow[CCl_4]{Br_2} CH_3-\overset{NO_2}{\overset{|}{C}}(NO_2)-CH_2CH_2Br,$$

$$AgOOCCH_2CH_2\overset{NO_2}{\overset{|}{C}}(NO_2)-CH_2CH_2COOAg \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2\overset{NO_2}{\overset{|}{C}}(NO_2)-CH_2CH_2Br.$$

Scribner[158] showed that perfluoro-carboxylic acids are converted into nitroperfluoro-alkanes under the action of nitrogen dioxide:

$$C_7F_{15}COOH \xrightarrow{NO_2} C_6F_{13}NO_2 + C_7F_{15}NO_2.$$

8. SYNTHESIS OF γ-BROMODINITRO-COMPOUNDS

Novikov et al.[159] developed a new method for the synthesis of γ-bromodinitro-compounds, which consists in the reaction of the mercury-derivatives of nitro-alkanes with bromine:

$$(NO_2)_2CHCH_2CH_2HgCl + Br_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} (NO_2)_2CHCH_2CH_2Br + HgBrCl,$$

1-Bromo-3,3-dinitropropane, 1-bromo-2-methyl-3,3-dinitropropane, 1-bromo-3,3-dinitro-2-phenylpropane, 2-bromo-1-dinitromethylcyclopentane, and 2-bromo-1-dinitromethylcyclohexane have been obtained. The reaction involves a radical mechanism.

9. OTHER METHODS

When a stream of gaseous hydrogen chloride is passed through a mixture of β-nitro-alcohol and paraformaldehyde in concentrated hydrochloric acid, chloromethyl ethers of the β-nitro-alcohols are produced[160,161]:

$$R-\overset{R'}{\overset{|}{C}}(NO_2)-CH_2OH + (CH_2O)_x + HCl \rightarrow R-\overset{R'}{\overset{|}{C}}(NO_2)-CH_2OCH_2Cl,$$

where R = H or CH_3 and R' = CH_3 or C_2H_5. In the presence of sodium methoxide nitromethane adds to esters of $\alpha\beta$-unsaturated fluoro-substituted acids with formation of fluoronitro-compounds containing other functional groups[65]:

$$RCH{=}CHCOOC_2H_5 + CH_3NO_2 \xrightarrow{CH_3ONa} RCH(CH_2NO_2)CH_2COOC_2H_5,$$

where R = CF_3 or C_3F_7. Bromonitropentanone has been obtained by the addition of bromonitroform to methyl vinyl ketone[162].

Boyd and Hansen[163] obtained 1-iodo-2-methyl-2-nitropropane by refluxing 2-methyl-2-nitropropyl esters of arenesulphonic acids with sodium iodide in acetone:

$$RSO_3CH_2\overset{(CH_3)_2}{\overset{|}{C}}(NO_2) + NaI \rightarrow (CH_3)_2\overset{CH_2I}{\overset{|}{C}}(NO_2).$$

Under the action of nitrogen tetroxide in ether, the oxime of chloroacetone is converted into 1-chloro-2-nitro-2-nitrosopropane, which is oxidised by chromic acid to the *gem*-dinitro-compound[164]:

$$ClCH_2\underset{NOH}{\overset{\|}{C}}-CH_3 \xrightarrow{N_2O_4} ClCH_2-\overset{NO}{\overset{|}{\underset{NO_2}{\overset{|}{C}}}}-CH_3 \xrightarrow{[O]} ClCH_2-\overset{NO_2}{\overset{|}{\underset{NO_2}{\overset{|}{C}}}}-CH_3.$$

Nitrosoperhalogeno-alkanes, obtained by the irradiation of a mixture of nitric oxide and a monoiodoperhalogeno-alkane with ultraviolet light, are converted into halogeno-nitro-compounds on oxidation with Cr_2O_3, PbO_2, or Mn_2O_7:[165]

$$RCF_2I + NO \rightarrow RCF_2NO \xrightarrow{O} RCF_2NO_2,$$

where R = Cl, CF_3, or C_2F_5.

Knunyants and coworkers[166] obtained esters of α-nitro-perfluoropropionic acid by the action of nitrogen tetroxide on esters of α-nitrosoperfluoropropionic acid:

$$CF_3\underset{NO}{\overset{|}{C}}F-COOR + N_2O_4 \rightarrow CF_3\underset{NO_2}{\overset{|}{C}}F-COOR + N_2O_3.$$

Nitro-alcohols react with trichloroacetonitrile in the presence of hydrogen chloride or bromide with formation of the hydrohalides of the corresponding trichloronitroalkyl-acetimidates. On decomposition, the latter yield halogeno-nitro-alkanes[167]:

$$CCl_3C{\equiv}N + HOCH_2CH_2NO_2 \rightarrow CCl_3\underset{NH\cdot HX}{\overset{\|}{C}}-OCH_2CH_2NO_2 \rightarrow CCl_3CONH_2 + XCH_2CH_2NO_2$$

By this method 1-chloro-2-nitroethane and 1-bromo-2-nitroethane have been obtained from nitroethanol and 1-chloro- and 1-bromo-2-nitropropane from 2-nitropropanol.

III. CHEMICAL PROPERTIES OF HALOGENONITRO-COMPOUNDS

1. REACTIONS WITH PARTICIPATION OF THE HALOGEN ATOM

a. Dehydrohalogenation

The dehydrohalogenation of halogenonitro-compounds to form nitro-olefins can be achieved either by pyrolysis or by treatment with basic reagents. Gold[168,169] pyrolysed β-chloronitro-compounds in the gas phase; it is best to carry out the process in the presence of catalysts [for example, $CaCl_2$, $CaCO_3$, $Ca_3(PO_4)_2$, $CaSO_4$, $Al(SO_4)_3$][168-170], which partially reduces the reaction temperature and increases the yields of nitro-olefins:

$$RCHCH_2NO_2 \rightarrow RCH{=}CHNO_2 \ .$$
$$\quad\ Cl$$

Spontaneous thermal dehydrohalogenation takes place when the products of the addition of nitryl chloride to styrene[3] or acrylic acid[12] are heated:

$$C_6H_5CH(Cl)CH_2NO_2 \rightarrow C_6H_5CH{=}CHNO_2 \ ,$$
$$NO_2CH_2CH(Cl)COOH \rightarrow NO_2CH{=}CHCOOH \ .$$

A convenient method for the dehydrohalogenation of β-halogenonitro-compounds consists in the treatment of the latter with basic reagents: alkalis[45,171], alkali metal acetates[8,12,45,172-175], and organic bases[10,12,45,176]. The dehydrohalogenation takes place more readily when the halogen (chlorine) atom is attached to a primary carbon atom, as, for example, in chloronitroethane. The dehydrohalogenation of 2-chloro-1-nitrobutane is slower. That of 2-chloro-3-methyl-1-nitrobutane is even more difficult[8]. Perekalin and Lerner[177] obtained 1,4-dinitrobutadiene by the dehydrochlorination of the corresponding dichloro-derivative with lead acetate:

$$O_2NCH_2CH(Cl)CH(Cl)CH_2NO_2 \rightarrow NO_2CH{=}CHCH{=}CHNO_2 \ .$$

2-Nitrobuta-1,3-diene has been obtained from 1-chloro-2-nitro-3-butanol and 1,3-dichloro-2-nitrobutane by the treatment of the mixture with potassium hydroxide[132].

Nitro-alkadienes are readily formed on dehydroiodination of the products of the addition of N_2O_4 and I_2 to diene hydrocarbons in the presence of a solution of lead acetate in glacial acetic acid[178]:

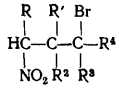
$$RCHI{-}CR'{=}CH{-}CH_2NO_2 \rightarrow R{-}CH{=}CR'{-}CH{=}CHNO_2 \ .$$

In the dehydrohalogenation of compounds in which the halogen and the nitro-group are further away than in β-halogenonitro-compounds, it is necessary to use strong bases, for example, sodium alkoxides[155]:

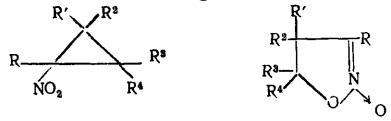
$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2Br \xrightarrow{NaOCH_3} CH_3\overset{NO_2}{C}{=}CH_2 \ .$$

On elimination of hydrogen halides from γ-halogenonitro-alkanes, nitrocyclopropanes have been obtained[179-185].

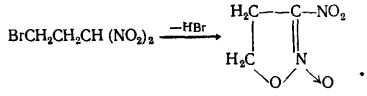
Koler and later Smith[179,180,184] showed that γ-bromo-nitro-compounds of the type



where R = $R^{1,2,3}$ = H, alkyl, or aryl and $R^4 = \diagdown C{=}O$ or -COAr, eliminate hydrogen bromide in an alkaline medium and form either the corresponding nitrocyclopropane derivatives or the isomeric isoxazoline *N*-oxides, depending on the structure of the starting material:



Intramolecular *O*-alkylation, which leads to the formation of 3-nitroisoxazoline-*N*-oxides under the action of alkaline reagents, is characteristic of γ-bromodinitro-compounds containing terminal *gem*-dinitro-groups[186]:



3-Nitro-2-isoxazoline has been obtained by treating 1-halogeno-3-nitropropanes with alkali metal nitrites[187]. Recently Bay[182,183] patented the synthesis of nitrocyclopropane by the dehydrohalogenation of 1-halogeno-3-nitropropanes under the action of sodamide in liquid ammonia or alkali metal carbonates and bicarbonates.

b. Reactions Involving the Substitution of the Halogen Atom

β-Halogenonitro-compounds readily react with aniline and its derivatives[3,7,8,53,188] forming *N*-nitroalkylanilines:

$$R{-}CHCl{-}CH_2NO_2 + C_6H_5NH_2 \rightarrow C_6H_5NH{-}CH\!\!\begin{array}{l}\diagup CH_2NO_2\\ \diagdown R\end{array} + HCl \ .$$

In the case of dichloronitropropane both halogen atoms are substituted[8]:

$$CH_2Cl{-}CHCl{-}CH_2NO_2 + 2NH_2C_6H_5 \rightarrow C_6H_5NHCH_2{-}\underset{NHC_6H_5}{\underset{|}{CH}}{-}CH_2NO_2 \ .$$

When 2,3,3,3-tetrachloro-1-nitropropane reacts with ammonia, *p*-toluidine, and phenylhydrazine, the products are the corresponding 2-amino-derivatives[189]. The study of the hydrolysis of β-halogenonitroalkanes with aqueous solutions of alcohol and dioxan showed that the reaction takes place by an S_N2 nucleophilic mechanism[8,134,190-193] with formation of nitro-alcohols:

$$\begin{array}{l}R\\ R'\end{array}\!\!\diagup CCl{-}CH_2NO_2 + H_2O \longrightarrow \begin{array}{l}R\\ R'\end{array}\!\!\diagup C{-}CH_2NO_2 + HCl \ ,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown OH$$

where R = H, C_2H_5, or iso-C_3H_7 and R′ = H or CH_3. The rate of hydrolysis depends on the nature of the carbon atoms to which the halogen is attached, decreasing on going from a primary to a tertiary carbon atom, as clearly illustrated by the following data[8]:

	Hydrolysis rate constant	
	in 75% ethanol	in 75% dioxan
$ClCH_2CH_2NO_2$	7.15×10^{-5}	5.27×10^{-5}
$H_3C{>}CH{-}CHClCH_2NO_2$ (H_3C)	2.27×10^{-5}	1.30×10^{-5}
$CH_3CH_2{>}CCl{-}CH_2NO_2$ (H_3C)	0.25×10^{-5}	0.21×10^{-5}

The halogen atom in the γ-position relative to the nitro-group is less mobile. Thus, whereas both chlorine atoms of 2,2-dichloro-1-nitroethane are readily substituted during hydrolysis, in 2,3-dichloro-1-nitropropane only the chlorine atom in the β-position is hydrolysed[8]:

$$O_2NCH_2{-}CHCl_2 \xrightarrow{2H_2O} O_2NCH_2CH(OH)_2 \xrightarrow{-H_2O} O_2NCH_2CHO,$$

$$O_2NCH_2{-}CHCl{-}CH_2Cl \xrightarrow{H_2O} O_2NCH_2\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2Cl.$$

When acetate salts react with halogenonitro-alkanes, it is possible to obtain the acetates derived from the corresponding nitro-alcohols[8,156,194]:

$$\rangle CCl{-}CH_2NO_2 \xrightarrow[CH_3COOH]{CH_3COOK} \rangle \underset{\displaystyle OCOCH_3}{\underset{|}{C}}{-}CH_2NO_2,$$

$$BrCH_2CH_2{-}\underset{\displaystyle NO_2}{\underset{|}{C}}{-}CH_2CH_2Br \xrightarrow[CH_3COOH]{CH_3COOAg} CH_3COOCH_2CH_2\underset{\displaystyle NO_2}{\underset{|}{C}}{-}CH_2CH_2OCOCH_3.$$

The reaction of β-chloronitro-compounds with mecarptans and their derivatives in the presence of sodium leads to the formation of sulphides[129,130]:

$$CH_3CHClCH_2NO_2 + HSCH_2CH(OC_2H_5)_2 \xrightarrow{Na} O_2NCH_2CH(CH_3)SCH_2CH(OC_2H_5)_2.$$

c. Dehalogenation

The dehalogenation of halogenonitro-alkanes has been little investigated. Only two reactions have been described in the literature: on heating above 120°C, 1,2-dibromo-1,2,2-trichloronitroethane decomposes with elimination of bromine[85]; on being refluxed with potassium cyanide, 1,2-dibromo-2-phenylnitroethane is converted into β-nitro-styrene[195]:

$$C_6H_5CHBr{-}CHBrNO_2 \rightarrow C_6H_5CH{=}CHNO_2.$$

2. REACTIONS WITH PARTICIPATION OF THE NITRO-GROUP

1. Reduction

Various methods may be used to convert halogenonitro-compounds into the corresponding aminohalogeno-derivatives. Konovalov[107] identified the nitro-derivatives which he obtained by reduction to the amines with zinc and hydrochloric acids. The reduction with iron and hydrochloric acid is also successful[139]:

$$NO_2C(CH_2Cl)_3 + Fe + HCl \rightarrow H_2NC(CH_2Cl)_3.$$

Another reagent used to convert halogenonitro-compounds into halogeno-amines is aluminium amalgam[133,188]. A number of investigators obtained aminohalogeno-compounds from the corresponding nitro-derivatives by reducing the latter with stannous chloride and hydrochloric acid[6,10,133,139,196].

Certain halogenonitro-compounds have been converted into halogeno-amines by catalytic hydrogenation over Raney nickel[8,55,65,67,197,198]. Hydroxylamines are then formed together with the amines. It has been mentioned that certain fluoronitro-compounds can be converted into amino-compounds with the aid of lithium aluminium hydride without affecting the C–F bond[57]. The electrolytic reduction of chloronitro-compounds to chloroalkylamines in aqueous alcohol in the presence of sulphuric acid has been reported[8].

When 6-chloro-5-nitrodec-5-ene is hydrogenated over PtO_2 in acetic acid in the presence of sodium acetate, simultaneous conversion of the nitro-group into NHOH and the replacement of the chlorine atom by hydrogen takes place[15]. Bromine atoms are replaced by hydrogen together with the reduction of the nitro-group in the hydrogenation of 1,2-dibromo-1-nitro-2-phenylethane over a palladium catalyst[148]:

$$C_6H_5CHBrCH(Br)NO_2 \xrightarrow{H_2} C_6H_5CH_2CH_2NH_2.$$

For the reduction of halogenonitro-compounds, see also the review of Novikov et al.[199]

b. The Effect of Mineral Acids

Under the action of mineral acids, halogenonitro-alkanes are converted into the corresponding halogeno-derivatives of carboxylic acids[19-22,105,200]. This reaction is so characteristic of fluoronitro-alkanes that it may serve as a convenient method for the synthesis of fluoro-carboxylic acids[200]:

$$-\underset{\displaystyle F}{\underset{|}{C}}{-}CH_2NO_2 \xrightarrow{H_2SO_4} -\underset{\displaystyle F}{\underset{|}{C}}{-}COOH.$$

When β-halogenonitro-alkanes are treated with aliphatic alcohols in the presence of strong acids (hydrochloric, sulphuric, and phosphoric), esters are produced[201]:

$$(CH_3)_2CClCH_2NO_2 + CH_3OH \xrightarrow{H_2SO_4} (CH_3)_2CClCOOCH_3.$$

When salts of the aci-forms of halogenonitro-alkanes are allowed to react with acids, halogeno-aldehydes are produced[109,121]:

$$NaOON{=}CHCH_2CH_2CHCl \xrightarrow[-15°]{H_2SO_4} CHClCH_2CH_2CHO.$$

3. OTHER REACTIONS

a. Reactions Involving a Mobile Hydrogen Atom

Reactions associated with the mobility of hydrogen atoms in the α-position relative to the nitro-group are characteristic of halogenonitro-alkanes as well as unsubstituted nitro-alkanes. Thus in the study of the condensation of trifluoro- and tetrafluoro-nitroethane with formaldehyde in the presence of alkalis, Knunyants et al.[198] obtained a good yield of fluoronitro-alcohols:

$$CF_3{-}CH_2NO_2 + 2CH_2O \xrightarrow{NaOH} CF_3{-}\underset{\displaystyle CH_2OH}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}{-}NO_2.$$

Chloronitro-alkanes enter into a similar condensation with formaldehyde in the presence of potassium carbonate[200]:

$$Cl_3CCHR'CH(NO_2)R + CH_2O \xrightarrow{K_2CO_3} Cl_3CCHR'\underset{\displaystyle CH_2OH}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}NO_2,$$

where R = H or CH_3 and R′ = OCH_3, OC_2H_5, C_2H_5, or C_4H_9. When the reaction is carried out in an alcoholic medium, the corresponding ethers are formed in both cases.

The "mobile" hydrogen atom is readily substituted by halogens[77]:

$$CF_3CHCH_2NO_2 \xrightarrow{Br_2} \underset{OH}{CF_3CH}-\underset{OH\ \ Br}{CHNO_2}.$$

When aryldiazonium salts react with acetates derived from halogenonitro-alcohols, diazotisation takes place[202]:

$$RCCl_2CH(OCOCH_3)CH_2NO_2 \xrightarrow{ArN_2^+} RCCl_2CH(OCOCH_3)C(NO_2)=NNHAr,$$

where R = Cl or CH_3CHCl.

b. Reactions with Formation of New C–C Bonds

Sayles and Degering[120] carried out the condensation of 4-chloro-1-nitrobutane with ethyl acetoacetate in the presence of sodium:

$$O_2N(CH_2)_4Cl + CH_3COCH_2COOC_2H_5 \xrightarrow{Na} O_2N(CH_2)_4CH(COCH_3)COOC_2H_5.$$

2-Chloro-1-nitropropane reacts with benzene in the presence of aluminium chloride[203]:

$$CH_3CHClCH_2NO_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5-CH\begin{matrix}CH_3\\CH_2NO_2\end{matrix}.$$

IV. APPLICATIONS OF HALOGENONITRO-COMPOUNDS

Compounds which contain both halogen atoms and nitro-groups are of definite interest because of their high physiological activity[200]. There have been a number of studies where it was shown that chloronitro-compounds can be used as insecticides[18,204-206], fungicides[57,71], bactericides[58,71,207], miticides[194], and herbicides[71].

When products of the addition of alcohols to β-(trichloromethyl)nitroethylene are reduced, amines are formed, some of which can be used as antispasmodic agents[196].

2-Chloro-1-nitro-olefins have been patented as fumigants, selective extracting agents, cellulose solvents, and varnish components[94,135].

Krug and Elmer[207] took out a patent for the application of the compounds $Cl_3CCH(R)C(R^1)(R^2)NO_2$ (where R = H or acyl containing 2–3 carbon atoms and R^1 and R^2 = H, CH_3, or C_2H_5) as additives (in amounts of 0.05–15%) to greases for gas-turbine engines. The same compounds are used for the dilution and dispersion of oils[208]. The application of bromonitro-alkanes and bromonitro-alkenes as additives to motor fuel has been mentioned[209].

Halogenonitro-alkanes are used as solvents[24] and additives to resin adhesives[111].

The application of 3,3,3-trichloro-1-nitropropane as a solvent for the copolymers of acrylonitrile with vinyl acetate and vinylpyridine in the dyeing of the polymeric products by organic dyes has been described[197].

The chloro-derivatives of 2,2-dinitropropanol and 2,2-dinitropropanediol have been proposed as plasticisers, solvents, and explosive components[148].

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The Chemistry of Acyl and Sulphonyl Isocyanates, Isothiocyanates, and Isoselenocyanates

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The review presents the latest advances in the chemistry of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates. All the methods for the preparation of these compounds are examined and treated systematically. Their reactions and their physical properties are described and the problems of their structure and isomerisation are discussed. In conclusion the available literature data on the practical importance and applications of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates are presented.

CONTENTS

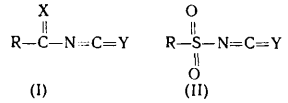
I.	Introduction	363
II.	Methods of preparation of acyl isocyanates, isothiocyanates, and isoselenocyanates	364
III.	Physical properties	365
IV.	The structure and isomerisation of acyl isocyanates, isothiocyanates, and isoselenocyanates	366
V.	Chemical reactions of acyl isocyanates, isothiocyanates, and isoselenocyanates	366
VI.	Applications of acyl isocyanates, isothiocyanates, and isoselenocyanates	371

I. INTRODUCTION

Organic isothiocyanates and isocyanates, first obtained towards the end of the last century, are assuming increasing importance at the present time. The enormous interest in this class of compounds is due to the fact that, by virtue of their reactivity, they have become important starting materials and intermediates for the synthesis of a wide variety of organic compounds, many of which have found practical applications. Organic isocyanates are essential for the synthesis of polymeric materials, synthetic fibres, medicinal preparations, insecticides, herbicides, fungicides, nematocides, photographic materials, and many other products.

In 1964 an International Symposium was held in Czechoslovakia on the chemistry of isocyanates [1]. Novel synthetic methods have been described in papers published recently[2-5] and new synthetic and practical applications have been found for organic isocyanates, isothiocyanates, and thiocyanates[6-7]. Reviews of the chemistry of isocyanates have been published[8-10].

The data on acyl isocyanates, isothiocyanates, and isoselenocyanates are scattered in many sources and information about them has not been compiled. The present review is an attempt to fill this gap. It deals with new data on the structure, methods of preparation, properties, and practical applications of acyl isocyanates, isothiocyanates, and isoselenocyanates, thioacyl isocyanates, sulphonyl isocyanates, and sulphonyl isothiocyanates with the general formulae (I) and (II):



(I) (II)

where X and Y can have the following significance: X = Y = O, X = Y = S, X = Y = Se, X = O and Y = S or Se, and X = S and Y = O or Se; R may be a halogen, alkyl, aryl, or an alkoxy- aryloxy-, or dialkylamino-group, etc.

The chemical properties of sulphonyl isocyanates [(II), Y = O] have been examined in Ulrich's review[10]. We shall deal only with those data on this class of compounds which were not included in Ulrich's review, but which are nevertheless of considerable interest.

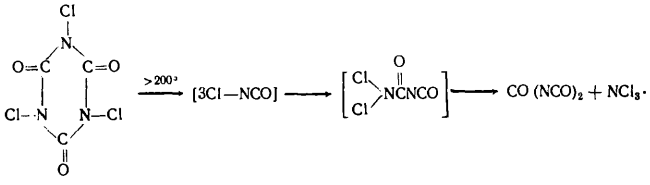
Of the two types of acyl isocyanates and isothiocyanates examined here, the first has been known for a long time, but recently there has been an increase of interest in these compounds. The chemistry of thioacyl isocyanates of the type R–C(=S)–N=C=O began to be studied in the last 4–5 years, while thioacyl isothiocyanates R–C(=S)–N=C=S and thioacyl isoseleno-

while thioacyl isothiocyanates R–C(=S)–N=C=S and thioacyl isoselenocyanates R–C(=S)–N=C=Se are still unknown. Acyl isoselenocyanates of the type R–C(=O)–N=C=Se have not been obtained in a pure form. Their existence has been demonstrated by conversion into selenourea derivatives. The first representatives of sulphonyl isothiocyanates $R-SO_2N=C=S$ have been obtained recently.

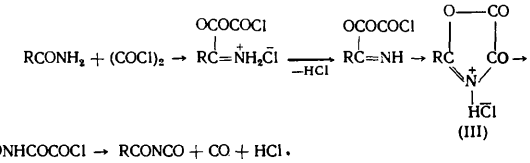
The review deals with papers published up to 1st June, 1967.

II. METHODS OF PREPARATION OF ACYL ISOCYANATES, ISTHIOCYANATES, AND ISOSELENOCYANATES

I. Carbonyl isocyanates. The simplest compound of this series, carbonyl diisocyanate O=C=N–C(=O)–N=C=O, was first obtained in 1966 by the thermal decomposition of trichloroisocyanuric acid at atmospheric pressure[11]. The reaction takes place via the intermediate formation of chloroisocyanate and *N*-dichloro-*N*-carbonylurea[12]:

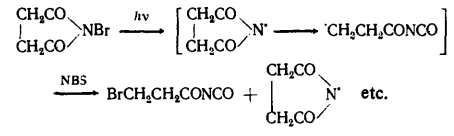


The corresponding chlorocarbonyl isothiocyanate ClCONCS and carbonyl di-isothiocyanate $CO(NCS)_2$ have not so far been obtained in a pure form. Their existence has been confirmed indirectly by the reactions of thiophosgene with lead thiocyanate, with subsequent conversion into thiourea derivatives[13,14]. The simplest acyl isocyanates have been obtained from the chlorides and salts of cyanic acid[15-24]. In recent years more convenient methods have been developed for the synthesis of acyl isocyanates. Recently a new and novel method has been proposed[25] for the synthesis of acyl isocyanates from unsubstituted amides and oxalyl chloride in dichloroethane with prolonged refluxing:



A ccording to the mechanism suggested for this reaction, *O*-acylation takes place in the first stage and is followed by intramolecular cyclisation with elimination of hydrogen chloride and the formation oxazolidin-4, 5-dione derivatives (III). On prolonged boiling, the latter are converted into acyl isocyanates with elimination of carbon monoxide and hydrogen chloride. In these reactions aromatic amides give yields of carbonyl isocyanates of 56–96%. Aliphatic amides react with somewhat greater difficulty, the yields of carbonyl isocyanates being 31–67%. The reaction of the amide of cyclopropanecarboxylic acid with oxalyl chloride takes place with opening of the cyclopropane ring and the formation of γ-chlorobutyryl isocyanate $ClCH_2CH_2CH_2CONCO$.[26] The possibility of preparing acyl isocyanates from acid amides and phosgene is mentioned in the patent of Waltmann and Wolf[27].

A method of preparation of acyl isocyanates by the rearrangement of cyclic *N*-bromo-imides was proposed by Johnson[28] and Martin[29]. Under the action of a catalyst (benzoyl peroxide, illumination) and in the presence of allyl halides, *N*-bromosuccinimide (NBS) forms the succinimide radical, which isomerises to the radical $^{\bullet}CH_2CH_2CONCO$, the latter being converted into β-bromopropionyl isocyanate under the action of NBS:



It has been shown[30] that this reaction does not take place with *N*-chloro- and *N*-iodo-succinimides but takes place smoothly in the case of *N*-bromoperfluoroglutarimine in the reaction with fully fluorinated olefins in the presence of benzoyl peroxide[31].

Acyl isocyanates are formed in high yields (greater than 90%) in the reaction of acid chlorides with isocyanic acid in the presence of tertiary amines (B)[32]:

$$RCOCl + HNCO + B \rightarrow RCONCO + BH^+Cl^- .$$

A wide variety of acyl isocyanates derived from carboxylic acids and mono- and di-isocyanates of silicon $[R_nSi(NCO)_{4-n}]$ and phosphorus $[R_nP(NCO)_{3-n}]$ derivatives have been obtained by this method.

Azidoformyl isocyanate has been obtained by the slow decomposition of oxalyl diazine[33]:

$$(N_3CO)_2 \xrightarrow[-N_2]{} N_3CONCO .$$

The formation of arylaminoformyl isocyanate has been observed in the decomposition of the azides of aryloxamic acids in the presence of aromatic amines[34].

2. Carbonyl isothiocyanate. The first representative of acyl isothiocyanates was synthesised from acid chlorides and thiocyanate salts as early as the 1880's. In most cases the reaction was carried out in inert solvents[35,47]. Later acetonitrile and acetone began to be used[36-44]. So far this is the only method for the preparation of acyl isothiocyanates.

By the reaction of the chlorides of arylazochloroacetic acids with sodium thiocyanate, the corresponding isothiocyanates of arylazochloroacetic acids were synthesised in high yields[42]:

$$ArNHN=C(Cl)COCl + NaSCN \rightarrow ArNHNC(Cl)CONCS .$$

The carbonyl isothiocyanates of the furan[39,43,44], pyridine[45], and pyrazolone[14] series have been synthesised by the reaction of acyl chlorides with thiocyanate salts. Carbonyl isothiocyanates have been obtained by the reaction of acylamino-carboxylic acids with the diphenyl ester of isothiocyanatophosphoric acid in the presence of triethylamine in acetonitrile[46]. This reaction is of exceptionally great importance in the synthesis of peptides. The formation of ethoxycarbonyl isothiocyanate was observed on heating *NN*- diethoxycarbonylthiourea up to the melting point.

Carbamoyl isothiocyanate can be obtained by the reaction of thiocyanic and isocyanic acids at a low temperature[48,49].

3. Thiocarbonyl isocyanates. These compounds have been investigated only in recent years [50-53]. So far however they have not been isolated in a pure form because of their exceptional reactivity. Their formation and existence in solutions have been demonstrated experimentally. Thiocarbonyl isocyanates are obtained by the thermal degradation of thiazolidin-4, 5-dione, which can in turn be synthesised by the reaction of thioamides with oxalyl chloride [54].

4. Carbonyl isoselenocyanates. These compounds were synthesised for the first time in 1937 by the reaction of acid chlorides with potassium selenocyanate in acetone solution [55,56]:

$$RCOCl + KSeCN \rightarrow RCONCSe + KCl.$$

However, they have not been isolated in pure form. Their existence has been demonstrated by conversion into the corresponding carbonylselenoureas. When an attempt was made to prepare the isoselenocyanates of arylazochloroacetic acid, the corresponding selenocyanates were isolated [42].

5. Sulphonyl isocyanates. Recently Smith and coworkers [57] put forward a method for the preparation of organic disulphonyl isocyanates by direct combination of phosgene with disulphonamides in nitrobenzene at 170–180°C. The yields are 54–67%:

$$R(SO_2NH_2)_2 \xrightarrow[170-180^\circ]{COCl_2} R(SO_2NCO)_2,$$

where R= $-(CH_2)_4-$, $-(CH_2)_6-$, or 1,5-naphthyl.

Ulrich and coworkers [58] synthesised a number of arylsulphonyl isocyanates in high yields by the reaction of arylsulphonamides with an excess of phosgene in the presence of butyl isocyanate as the catalyst. Treatment of *p*-aminobenzenesulphonamide with phosgene in nitrobenzene leads to various products, depending in the reaction temperature: *p*-(chloroformamide) benzenesulphonamide formed at 0°C is converted into *p*-isocyanatobenzenesulphonamide at 90°C and into *p*-isocyanatobenzenesulphonyl isocyanate at 150°C [57]. Benzenesulphonamide reacts with phosgene in 1, 2, 4-trichlorobenzene solution in an atmosphere of nitrogen to form benzenesulphonyl isocyanate [59]. When benzenesulphonamide was allowed to react with a four-fold excess of axalyl chloride in dichlorobenzene solution, benzenesulphonyl isocyanate was obtained in 81% yield [60].

Recently a method has been proposed for the preparation of sulphonyl isocyanates from 1-arylsulphonyl-3-alkylureas and alkylenedi(arylsulphonyl)ureas and phosgene at 120–180°C in non-polar solvents [58]:

$$RC_6H_4SO_2NHCONHAlk \xrightarrow[-HCl]{COCl_2} \underset{90\%}{RC_6H_4SO_2NCO} + AlkNCO.$$

Not long ago a method was described [61] for the preparation of sulphuryl di-isocyanate and chlorosulphuryl cyanate by the reaction of cyanogen chloride with sulphur trioxide at 200–250°C in the presence of iron, cobalt, nickel, chromium, molybdenum, copper, and aluminium salts:

$$ClCN + SO_3 \xrightarrow{200-250^\circ} ClSO_2NCO + SO_2(NCO)_2.$$

Chlorosulphonyl isocyanate can be completely converted by pyrolysis into sulphuryl di-isocyanate. The method proposed is dinstinguished by its simplicity, high yields of the final products, and the possibility of achieving a continuous synthesis.

6. Sulphonyl isothiocyanates. When dipotassium salts of sulphonyliminodithiocarbonic acids [62-66] were allowed to react with phosgene in benzene, carbon tetrachloride, or methylene chloride at a low temperature, sulphonyl isothiocyanates were obtained in yields up to 88% [65,66]:

$$RSO_2NC(SK)_2 + COCl_2 \rightarrow RSO_2NCS + COS + 2KCl,$$

where R=alkyl or aryl.

Phosgene can be replaced by the chloroformic ester, phosphorus pentachloride, thionyl chloride, and sulphuryl chloride [62-64]. On standing, sulphonyl isothiocyanates dimerise spontaneously.

Ulrich [67,68] proposed a method for the synthesis of sulphonyl isothiocyanates by the reaction of sulphonylthioureas and phosgene:

$$RSO_2NHCNHR + COCl_2 \rightarrow RSO_2NCS + RNCO.$$
$$\quad\quad\quad

asymmetric stretching vibrations of sulphonyl isocyanates differ little from those in the spectra of alkyl and aryl isocyanates.

Nevertheless we believe that in acyl isothiocyanates ($R-\overset{\overset{O}{\|}}{C}-N=C=S$ and $RSO_2N=C=S$) there is slight interaction (or inductive effect) between $R-C=O$, $-SO_2-$, and $-N=C=S$ groups. It is expressed in an increase of the proportion of the mesomeric dipolar structure $R-C(\bar{O})=\overset{+}{N}=C=S$, in an increase of the double-bond character of the bond involving the nitrogen atom, and in a slight displacement of the stretching-vibration bands of the N=C=S and C=O groups towards longer wave lengths. Thus, whereas the stretching vibration frequency $\nu_{(as)}$ for CH_3NCS is 2110 cm^{-1} it is 1980–1950 cm^{-1} for CH_3CONCS, 2095 cm^{-1} for C_6H_5NCS, 1970–1930 cm^{-1} for C_6H_5CONCS, and 1905 cm^{-1} for $C_6H_5SO_2NCS$. [10,73,76-76]

IV. THE STRUCTURE AND ISOMERISATION OF ACYL ISOCYANATES, ISOTHIOCYANATES, AND ISOSELENOCYANATES

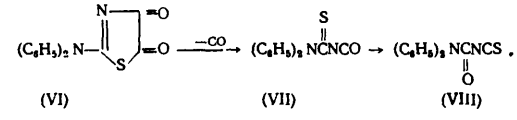
It is known that, in the synthesis of acyl isocyanates, isothiocyanates, and isoselenocyanates by the double decomposition reaction of acid halides with isocyanate, selenocyanate, and isothiocyanate salts, there is a possibility of the formation of compounds (IV) and (V):

$$\underset{}{AcHal} + MXCN \rightarrow \underset{(IV)}{AcNCX} + \underset{(V)}{AcXCN},$$

where M=K, Pb, Na, or NH_4 and X=O, S, or Se. The reasons for the preferential formation of compounds (IV) or (V) have not been adequately elucidated so far [79,80]. Some authors state that compounds (IV) form preferentially during the double decomposition process [81,82] while others isolated compounds (V) [83].

We believe that the preferential formation of acyl isothiocyanates relative to acyl thiocyanates is associated with the fact that, as a result of the mesomerism $^-S-C^-\equiv N \rightleftharpoons S=C=N^-$, it is easier for thiocyanate ions, on energy grounds, to form compounds (IV) rather than compounds (V) (according to Pauling [84], the energy of formation of the C–N bond is 67.7 kcal $mole^{-1}$, that of the C–S bond is 62 kcal $mole^{-1}$, the electronegativity of nitrogen is –3, and that of sulphur –2.5). Furthermore, there are literature data showing that the fraction of acyl thiocyanate which does form isomerises to acyl isothiocyanate under the action of thiocyanate salts [78].

The isomerisation of thioacyl isocyanate to acyl isothiocyanate was first observed for diphenylaminothiocarbonyl isocyanate obtained by the thermal decomposition of 2-diphenylaminothiazolidin-4,5-dione [51]:



(VI) (VII) (VIII)

Infrared absorption spectroscopic data showed that, in the decomposition of product (VI), there appears in the infrared spectrum an absorption band with $\nu_{(as)}$ (NCO)= 2230 cm^{-1}, which is characteristic of structure (VII). On further heating, the 2230 cm^{-1} band vanishes and is replaced by an absorption frequency at 1970 cm^{-1}, characteristic of the NCS group [compound (VIII)]. The mechanism of the conversion of compound (VII) into compound (VIII) proposed by the authors, including the formation of intermediates, was confirmed for other examples by chemical reactions involving tracer atoms. [53,85]

V. CHEMICAL REACTIONS OF ACYL ISOCYANATES, ISOTHIOCYANATES AND ISOSELENOCYANATES

Acyl isocyanates, isothiocyanates, and isoselenocyanates enter into the majority of chemical reactions characteristic of alkyl and aryl isocyanates, isothiocyanates, and isoselenocyanates. However, there are also differences, which are described below.

1. Reaction with Water and Alkalis

Carbonyl isocyanates react with water to form acid amides, carbon dioxide, and dicarbonyl ureas [18]. Carbonyl isothiocyanates are hydrolysed by water, also with formation of acid amides and carbon sulphide oxide [13]. They react more vigorously with alkalis, giving almost quantitative yields of acid amides. The hydrolysis of acyl isothiocyanates was investigated in detail by Elmore and Ogle [40,86]. The hydrolysis of sulphonyl isocyanates was studied recently by Smith [57]. By comparing the ease of hydrolysis of aliphatic and aromatic acyl isothiocyanates, Elmore and Ogle [87] established that phosphonyl isothiocyanates occupy an intermediate position between aliphatic and aromatic acyl isothiocyanates:

$$AlkCONCS > (RO)_2PONCS > ArCONCS.$$

2. Reactions with Aromatic and Aliphatic Alcohols and Mercaptans

Acyl isocyanates, isothiocyanates, and isoselenocyanates react with alcohols and mercaptans to form the corresponding urethanes, thiourethanes, and dithiourethanes. This reaction has been frequently studied with carbonyl isocyanates [26,88-92], carbonyl isothiocyanates [36,40,93,94], and sulphonyl isocyanates [59,95,96]. The preparation of urethanes by the reaction of carbonyl isocyanates with alcohols, glycols, and phenols constitutes a qualitative test for alcohols and phenols [88,89]. According to kinetic data, the formation of urethanes is a monomolecular reaction [93]. It takes place readily both at primary and sterically hindered alcohols and phenols [88,89,95]. The reaction of sulphonyl isocyanates with alcohols (2-methyl-2-propanol, 3-ethyl-3-pentanol) in toluene solutions takes place instantaneously even at 0°C.

3. Reactions with Ammonia, Amines, Aminonitriles, Amides, Substituted Hydrazines, Hydrazides, and Oximes

The reaction of acyl isocyanates, isothiocyanates, and isoselenocyanates with ammonia and amines has been thoroughly investigated and takes place smoothly both in polar solvents and in solvents of low polarity on heating [37,39-45,97-100]. The reactions of amines and diamines with carbonyl isocyanates [101-105], carbonyl isothiocyanates [86,97-100,106-117], thiocarbonyl isocyanates [52], carbonyl selenocyanates [55,118], and sulphonyl isocyanates [119-124] have been described.

Aliphatic and aromatic amines react with acyl isocyanates almost quantitatively. Aromatic polynitroamines do not enter into the condensation reaction [106].

Thiobenzoyl isocyanate does not react with ammonia and methylamine hydrochloride[52]. Amino-acids[40,86], carboxylic acid amino-esters[114], and heterocyclic bases[111,112] react similarly to aromatic amines. The acylureas and acyl thioureas obtained from them are widely used for the synthesis of heterocyclic compounds[111-114].

The mechanism of the reaction of acyl isocyanates and acyl isothiocyanates with amines was studied using as an example the reaction of sulphonyl isocyanates with primary and secondary amines in the presence of tertiary amines[119]. It has been shown that the mechanism proposed by Baker and Gaunt[125], according to which the reaction takes place via an intermediate donor–acceptor complex of the isocyanate with the tertiary amine, is entirely suitable for this process:

$$RSO_2NCO + R_3N \longrightarrow \left[RSO_2N=C-O^- \;\; \underset{NR_3^+}{} \right] \xrightarrow{R''NH_2} RSO_2NHCONHR''.$$

α-Aminonitriles and their substituted derivatives react with acyl isocyanates and acyl isothiocyan tes similarly to amines. The reaction usually leads to the formation of thioureas, thiazole, and mercaptoimidazole[126]. Aminoacetamide enters into similar reactions but less vigorously[127]. (Ethoxycarbonyl) carbonyl isothiocyanate reacts with α-amino-nitriles similarly to benzoyl isothiocyanate, with formation of thiazole and imidazole derivatives[128].

Tri(dimethylamino)phosphine reacts with benzoyl isothiocyanate to form the corresponding thiourea[129]. Similarly, dimethylsulphoxylidene reacts with acyl isocyanates and isothiocyanates to give dimethylsulphoxylideneureas and dimethylsulphoxylidenethioureas[130].

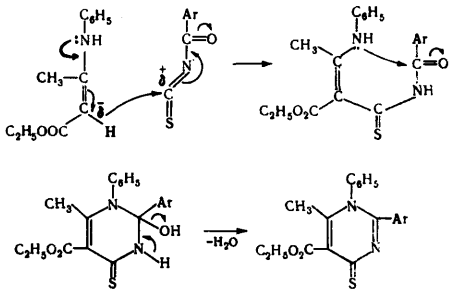
The reaction of acyl isocyanates with ureas and substituted thioureas in ether or benzene leads to the formation of biurets and thiobiurets RCONHCONHCNHR (where X= O or S) in high yields[16]. These compounds exhibit powerful physiological activity. Acyl isocyanates, isothiocyanates, and isoselenocyanates react with substituted hydrazines to form the corresponding 4-acyl-1-substituted semicarbazides and thiosemicarbazides[37,131-133] and selenosemicarbazides[134]. With thiocarbonyl isocyanate, substituted hydrazines form triazolone derivatives[52].

Unsubstituted hydrazine reacts with acyl isocyanates and isothiocyanates to form symmetrically substituted hydrazines[131] and sometimes, depending on the conditions, triazole derivatives[131]. The reaction of acyl isothiocyanates with acid hydrazides is similar to the reaction with substituted hydrazines; it has been investigated in detail using as an example the hydrazide of isonicotinic acid in alcohol, dioxan, and acetonitrile solutions. The resulting 1-isonicotinoyl-4-acylthiosemicarbazides exhibit high bacteriostatic activity[37,132,135].

The reaction of acetaldehyde-ammonia with carbonyl isothiocyanates was studied by Elmore and Ogle[136], who established that the product is 1,1-di[alkoxycarbonyl (thioureido)] ethane. The interaction of acyl isocyanates and isothiocyanates with oximes was investigated by Gheorghiu and coworkers[137,138]. However, the reaction mechanism was not elucidated. It has been shown that the reaction is exceptionally complicated, involving the formation of numerous products. Thus benzamide, benzonitrile, benzoylurea, benzoylcyanamide, carbon oxide sulphide, sulphur and other products have been isolated in the reaction of benzoyl isothiocyanate with aldoximes and ketoximes.

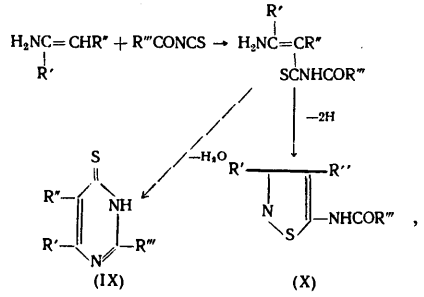
4. Reactions with Compound Containing an Active Hydrogen Atom

Acyl isocyanates and isothiocyanates react comparatively readily with organic compounds containing activated hydrogen atoms. An example is the reaction of acyl isothiocyanates with an $\alpha\beta$-unsaturated amino-ester, for example the β-anilinocrotonic ester[139]. It has been established that the primary product of this reaction is β-anilino-α-benzoyl thiocarbonyl crotonate[140]. However, when the latter is heated in ether or tetrahydrofuran, derivatives of 4-thiopyrimidine are obtained in yields up to 70%:



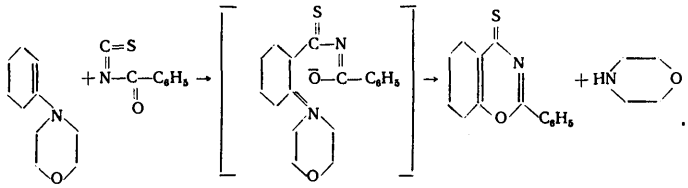
The reaction is general and can be applied both to $\alpha\beta$-unsaturated amino-esters and to various acyl isocyanates and isothiocyanates. The yield of the final product depends significantly on the nature of the substituent in the aromatic ring: electron acceptors increase and electron donors decrease the yield and favour the formation of side products.

In the reaction of carbonyl isocyanates with aliphatic amines, amino-esters, and diamines with the amino-group at the double bond, there is a possibility of the formation of pyrimidine (IX) and isothiazole (X) derivatives[141-144]:



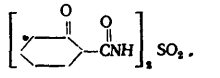
where R′ = NH_2, OC_2H_5.

Benzoyl isothiocyanate readily reacts with 1-morpholinylcyclohexene in chloroform to form 2-aryl-5,6,7,8-tetrahydro-1,3-benzoxazine-4-thione[145]:

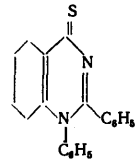


Similarly in the reaction with 1-morpholinylcyclohexene, sulphuryl di-isocyanate leads to the formation of the adduct

NN-di(2-morpholinyl-3,4,5,6-tetrahydrobenzoyl)sulphonamide, which is converted into *NN'*-di(2-oxohexahydrobenzoyl)sulphonamide on hydrolysis with 70% sulphuric acid[146]:

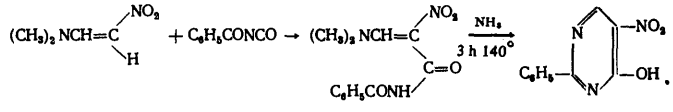


In a similar reaction with benzoyl isothiocyanate in ether 1-phenylaminocyclohexene gives 1,2-diphenyl-5,6,7,8-tetrahydroquinazolone-4-thione[140,147]:

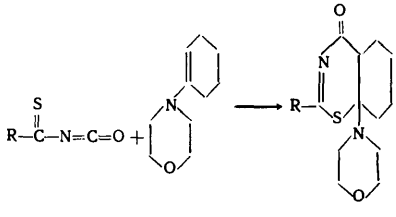


The above reactions involving the addition of acyl isocyanates and isothiocyanates to the β-carbon atom of primary and secondary enamines make possible the preparation by a new synthetic procedure of pyrimidine and quinazoline derivatives[147,148].

Acyl isocyanates readily add also to 1-dimethylamino--2-nitroethylene in benzene at 20°C with formation of *N*-benzoyl-β-dimethylamino-α-nitroacrylamide[149]. When the latter reacts with ammonia initially at 0°C and then at 140°C, it is converted over a period of 3 h into 4-hydroxy--5-nitro-2-phenylpyrimidine, which is otherwise difficult to obtain:



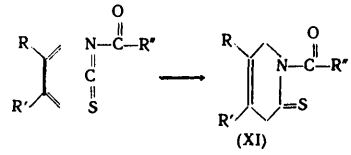
Thioacyl isocyanates react more vigorously with compounds containing active hydrogen atoms[151]. Thus, in the reaction of thioacyl isocyanates with 1-morpholinylcyclohexene in ether at 0°C and with 2,3-dihydropyran, the addition takes place in accordance with the 1,4-cycloaddition principle, with formation of 2-aryl-4a,5,6,7,8,8a-hexahydro-8a-morpholino-4*H*-1-benzothiazin-4-one,



and 2-aryl-8-oxa-1-thia-3-azabicyclo[4,4,0]dec-2-en-4-one.

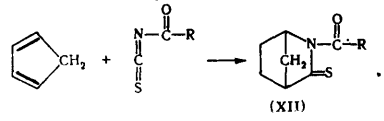
5. Acyl Isocyanates and Isothiocyanates in Diene Synthesis Reactions

The participation of acyl isocyanates and isothiocyanates in diene synthesis reactions has been investigated very little. The work of Arbuzov and Zobova deals with this question[150,151]. Using acetyl and benzoyl isocyanates and isothiocyanates as an example[150], they studied their interaction with a number of dienes: divinyl, isoprene, 2,3--dimethylbuta-1,3-diene, and cyclopentadiene. The reaction probably involves 1,4-addition with formation of 4(5)-substituted *N*-acyl-1,2,3,6-tetrahydro-2--thionopyridines (XI) in a yield of 40–45% in the presence of divinyl, isoprene, and 2,3-dimethylbuta-1,3-diene:



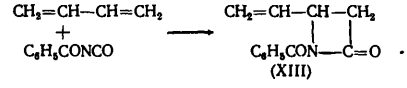
(XI)

and *N*-acyl-3-thiono-2-azabicyclo[2,2,1]hept-5-ene (XII) in a yield of about 50% in the presence of cyclopentadiene:



(XII)

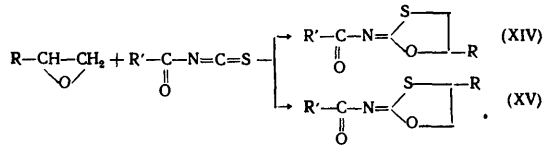
Benzoyl isocyanate reacts with 1,3-dienes to form 1,2--addition products[151] (XIII) in yields of 30–40%:



(XIII)

6. Reactions with Epoxides

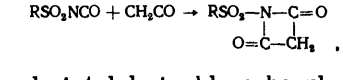
In contrast to other isothiocyanates[152,153], acyl isothiocyanates react with the double bond of the thiono-group C=S of the isothiocyanate[154,155] to form two five-substituted derivatives of 1,3-oxathiolane-(XIV)or(XV):



However, in the case of 2,3-epoxy-1-phenoxypropane the reaction with acyl isothiocyanate takes place with formation of compound (XIV) only, as demonstrated rigorously by synthesis. The formation of compound (XIV) can be explained by the fact that in most addition reactions the epoxy-ring is opened on the side of the unsubstituted carbon atom because of the steric hindrance due to substituents.

7. Reactions with Ketens

The reactions of acyl isocyanates and isothiocyanates with ketens have been almost not investigated. It has been established recently that keten reacts very readily with sulphonyl isothiocyanate to form the corresponding *N*-sulphonylazetidinediones[156]:



where R = phenyl, *p*-tolyl, *p*-chlorophenyl, *p*-fluorophenyl, etc, and if the products are unstable, polymers derived from the latter, of the type $[-COCH_2CONSO_2R]_n$, are formed. Usually the reaction takes place in ether or methylene chloride at a temperature between - 30° and - 10°C. Sulphonyl isocyanates also react readily with vinyl ethers, keten acetals[157], and olefins of the type, $[RCH{=}CR']_2S$ at 20–170°C.[158] Both di-isocyanate groups of di-isocyanates react with keten to form bis-*N*-sulphonylazetidines[156].

8. Reactions of Acyl Isocyanates with Orthocarbonic Esters

Recently Biener [159] described an interesting reaction of sulphonyl isocyanates with orthocarbonic esters. This reaction makes it possible to obtain yields up to 90% esters of *N*-sulphonyl-*N*-alkylcarbonic acids which cannot be obtained otherwise:

$$R''SO_2NCO + R'(COR)_3 \rightarrow R''SO_2N(R)CO_2R + R'COOR.$$

Usually the reaction takes place at a low temperature in methylene chloride or chloroform and virtually reaches completion in 1–2 h. In reactions with sulphonyl di-isocyanates, either one or two isocyanate groups may be involved, with formation of various products.

9. Acyl Isocyanates in the Grignard Reaction

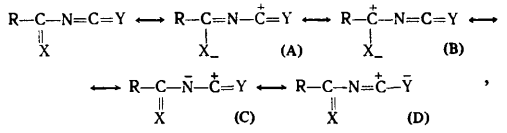
The Grignard reaction was studied in detail by McFarland between benzene- and *p*-toluene-sulphonyl isocyanates and alkyl- and aryl-magnesium bromides (or iodides) in ether at a low temperature. *N*-Sulphonamides are obtained in yields up to 88% when isocyanate or isothiocyanate is added to the Grignard reagent:

$$RSO_2NCO + R'MgX \xrightarrow[H^+,\ H_2O]{\text{ether}} RSO_2NHCOR'.$$

When the Grignard is added to the isocyanate or isothiocyanate, the reaction is accompanied by side processes and the yields of *N*-sulphonamides fall by a factor of 4–5. When the reaction is carried out with an excess of the Grignard reagent and the mixture is refluxed, the yield of the final product is appreciably reduced [160].

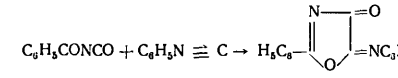
10. Acyl Isocyanates and Isothiocyanates in Reactions with Compounds Containing the C=N Bond

a. Reactions with isonitriles. The reactions of acyl isocyanates and isothiocyanates and thioacyl isocyanates with isonitriles and carbodi-imides can be regarded as dipolar 1,4-addition and dipolar 1,2-interaction [51,161]. In various reactions acyl isocyanates and isothiocyanates can be represented by dipolar structures:



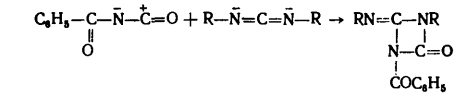
where Y, X=O, S, Se.

Benzoyl isocyanate reacts with phenylisonitrile in benzene with formation of 5-phenylimino-oxazolin-4-one in 96% yield:

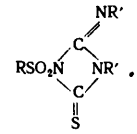


When isonitriles react with acyl isocyanates in the presence of carboxylic acids, intramolecularly acylated mixed amides of the type RNHCOCON(COR')COR", which are otherwise difficult to obtain, are formed in yields up to 90%. [162] Thiobenzoyl isocyanate and benzylmercapto-thiobenzoyl isocyanate react with the isonitrile in methylcyclohexane or toluene more vigorously, forming respectively 2-phenyl- and 2-benzylmercapto-5-phenylimino thiazolidin-4-one in 70–85% yield [51,53,161]. Di-isonitriles react with acyl isocyanates and isothiocyanates similarly, with formation of di-imino-thiazolin-4-ones [161,163].

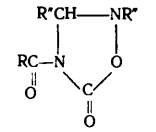
b. Reactions with carbodi-imides. It is known that compounds with cumulated double bonds (for example carbonylsulphonyl isocyanates and isothiocyanates) readily enter into dipolar 1,2-cycloaddition reactions. Thus benzoyl isocyanate reacts with carbodi-imide in a 1:1 benzene–ether mixture with formation of 4-imino--1,3-diazetidin-2-one in a yield up to 70% [53,161,164]:



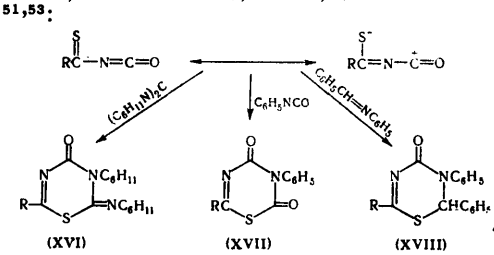
Under similar conditions [68,165] sulphonyl isothiocyanates give rise to quantitative yields of 2-imino-1,3-diazetidin-4--thione:



Another example of dipolar 1,2-addition may be the reaction of acyl isocyanates with *N*-ethylbenzaldoxime in a 1:1 benzene–ether solution, which leads to the formation of 1,2,4-oxadiazolidin-5-one in a yield up to 90% [161]:

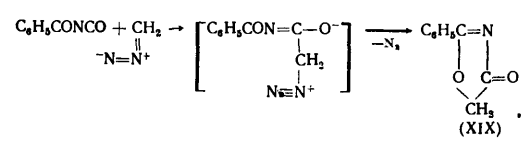


In view of the very pronounced nucleophilic properties of the sulphur atom in thioacyl isocyanates compared with the oxygen atom of acyl isocyanates, the former are more reactive. In addition reactions they probably have the dipolar structure (A) and this accounts for their interaction with carbodi-imides, isocyanates, and benzylideneamine by a 1,4-cycloaddition mechanism with formation of the corresponding substituted six-membered heterocyclic compounds—2-imino-1,3,5-thiadiazin-4-one (XVI), 1,3,5--thiadiazin-2, 4-dione (XVII), and 1,3,5-thiadiazin-4-one (XVIII) [51,53]:



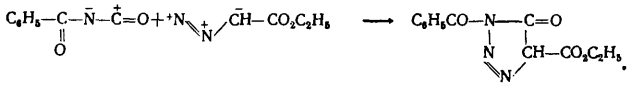
11. Reactions of Acyl Isocyanates and Isothiocyanates with Diazo-alkanes

The reactions of acyl isocyanates and isothiocyanates with diazo-alkanes began to be studied recently. It has been shown that benzoyl isocyanate reacts with diazomethane to form 2-phenyl-oxazol-4-one in yields up to 70% [166]. The mechanism of this reaction may be regarded as addition of diazomethane to the polarised carbonyl bond of the isocyanate in the first stage with subsequent elimination of nitrogen and formation of 2-phenyloxazol-4-one (XIX):

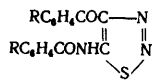


The structure of the latter has been demonstrated by hydrolysis and the formation of the amide of benzoylglycolic acid.

Benzoyl isocyanate reacts readily with ethyl diazoacetate, with formation of the ethyl ester of 1-benzoyl--1,2,3-triazol-5-one-4-carboxylic acid [167,168]:



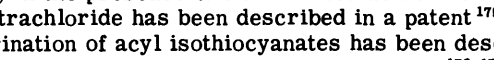
Acyl isothiocyanates react with diazomethane, ethyldiazoacetate, diazoacetamide, ω-diazoacetophenone etc. [168-172] with formation of 1,2,3-thiadiazole derivatives. Substituted ω-diazoacetophenone derivatives react with benzoyl isothiocyanate to form 5-acetamide-4-benzoyl--1,2,3-thiadiazole:



Usually these reactions take place at 100°C and are virtually complete in 30–120 min [172]. The nature of the substituent in the diazoacetophenone molecule has a significant influence on the rate of the addition reaction. With electron-acceptor substituents, the reaction takes place very slowly or not at all, while electron-donor substituents accelerate the process [170].

12. Reaction of Acyl Isocyanates and Isothiocyanates with Chlorine

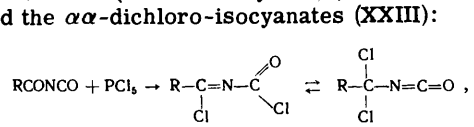
The chlorination of benzoyl isothiocyanates was first studied by Johnson and coworkers [173,174]. The chlorination of acyl isothiocyanates $CH_3(CH_2)_n$-CONCS (where n=2,6,10, 12, or 14) in the presence of titanium tetrachloride in carbon tetrachloride has been described in a patent [175]. The chlorination of acyl isothiocyanates has been described in detail in the papers of Derkach and coworkers [176,177], who established that the chlorination products are the sulphenyl chloride derivatives of the chlorides of N-acyliminocarbonic acids (XX) and the dichlorides of N-acyliminocarbonic acids (XXI):



The dichlorides (XXI) are valuable starting materials for the synthesis of new heterocyclic compounds [178].

13. Acyl Isocyanates and Acyl Isothiocyanates in Reactions with Phosphorus Pentachloride

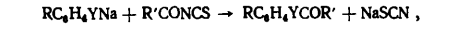
The reaction of acyl isocyanates with phosphorus pentachloride was studied only by Neidlein and coworkers [178-182]. On prolonged heating in chlorobenzene of benzoyl isocyanate and phosphorus pentachloride in proportions of 1 : 1, the chloride of α-phenyl-α-chloroalkylidene carbamic acid forms. Aliphatic acyl isocyanates react with phosphorus pentachloride to form an equilibrium mixture of the chlorides of N-(α-chloroalkylidene)carbamic acids (XXII) and the αα-dichloro-isocyanates (XXIII):



where R = $ClCH_2$, Cl_2CH, Cl_3C, etc. The mode of reaction was confirmed by infrared spectroscopy [181].

14. Acyl Isocyanates and Acyl Isothiocyanates in Alkoxycarbonylation Reactions

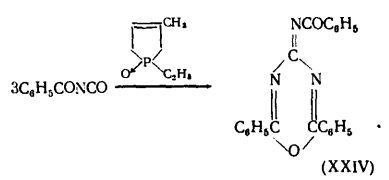
Acyl isothiocyanates readily enter into the alkoxycarbonylation of acylation reaction with phenoxides and phenyl sulphides. The presence in the phenoxide molecule of electronegative substituents facilitates the reaction [183]:



where Y = O or S and R′ = C_2H_5O, C_4H_9O, CH_3, C_6H_5, or C_2H_5S. It has been established that the acylating activity of acyl thiocyanates and isothiocyanates decreases in the series RCOSCN > RCONCS > ROCOSCN > ROCONCS > > RSCONCS. This reaction has found practical application in the synthesis of *OS*-di(alkoxycarbonyl)thiamine [78].

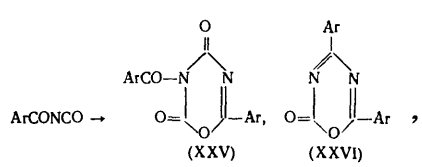
15. Dimerisation, Trimerisation, and Polymerisation of Acyl Isocyanates and Isothiocyanates

The first unsuccessful attempt to study the polymerisation of acyl isocyanates was undertaken in 1960. [184] The trimerisation of benzyol isocyanate under the action of a phospholene oxide in dry xylene with refluxing was studied by McGrew et al. [185]. On the basis of infrared absorption spectra and thermal and hydrolytic degradation of the reaction products, the authors attributed the structure of 4-benzoylimino-2,6-diphenyl-1,3,5-oxadiazine (XXIV) to the trimerisation product and proposed a mechanism for its formation:

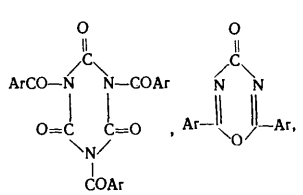


(XXIV)

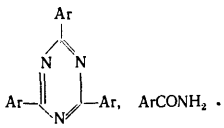
Japanese chemists [186,187] studied in detail the di- and tri-merisation of aroyl isocyanates in ether and cyclohexene in the presence of triethylamine, pyridine 1-oxide, and pyridinium salts as catalysts. They showed that the reaction is very complex. Depending on the conditions, the catalyst and the substituent in the aroyl isocyanate molecule, the products may be 5-aroyl-2-aryl-1,3,5--oxadiazin-4,6-dione (XXV), 2,4-diaryl-1,3,5-oxadiazin--6-one (XXVI), triaroyl isocyanurate (XXVII), 2,6-diaryl--1,3,5-oxadiazin-4-one (XXVIII), and also triaryl-s--triazine (XXIX) and aromatic acid amides (XXX):



(XXV) (XXVI)

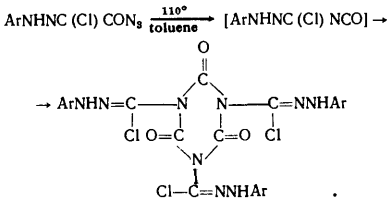


(XXVII) (XXVIII)



(XXIX) (XXX)

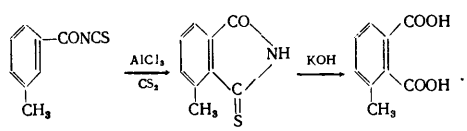
The present authors isolated the trimerisation products of arylazochloroacetyl isocyanates in an attempt to prepare the isocyanates of the arylhydrazones of chloroformaldehyde from arylazochloroacetyl azides [188,189]:



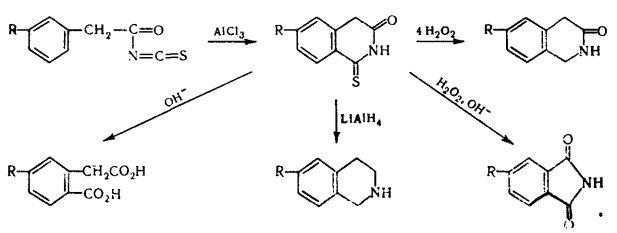
The isothiocyanates of iminocarboxylic acids readily dimerise in the light into quinazoline and *s*-triazine derivatives [190-192].

16. Acyl Isocyanates and Isothiocyanates in Intermolecular and Intramolecular Cyclisation Reactions

The intra- and inter-molecular cyclisation of acyl isothiocyanate was first studied in detail by Smith and Kan [193,194] and a novel method for the preparation of phenyl-substituted dicarboxylic acids was proposed on its basis:



It is noteworthy that the reaction does not take place with *p*-toluoyl, benzoyl, 3-methoxybenzoyl, 3,5-dimethoxybenzoyl, 3,4,5-trimethoxybenzoyl, and α-naphthoyl isothiocyanates. The cyclisation takes place smoothly when methyl groups are present in the *meta*-position with respect to the carbonyl isothiocyanate group (3-methyl, 3,5-dimethyl). Furthermore, it requires the presence of two free *ortho*-positions. When *m*-toluoyl isothiocyanate is used, the cyclisation takes place with formation of 2-methylphthalic acid only. The use of phenylacetyl isothiocyanate and its derivatives in a similar intramolecular cyclisation reaction opens up extensive possibilities for the synthesis of homophthalic acids and a number of heterocyclic compounds, in particular 1,2,3,4-tetrahydroisoquinoline and phthalimide:



In contrast to *m*-toluoyl isothiocyanate, *m*-tolylacetyl isothiocyanate cyclises exclusively in the para-position with respect to the methyl group with formation of 5-methyl-2a-thiohomophthalimide or 6-methyl-1-thio-1,2,3,4-tetrahydro-*2H*,*4H*-isoquinoline-1,3-dione†, 4-methylphthalimide and 4-methylhomophthalic acid being obtained from the latter.

3-Thienoyl isothiocyanate, βγ-saturated aliphatic carbonyl isothiocyanates and cyclohexen-1-ylacetyl isothiocyanate also undergo intermolecular cyclisation [193,194] Despite certain limitations, this reaction is of fundamental importance. It makes it possible to obtain a number of heterocyclic compounds, and from the latter substituted *ortho*-dicarboxylic acids, which are difficult to obtain.

17. Other Reactions of Acyl Isocyanates and Isothiocyanates

In 1966 Neidlein [195] described the reaction of carbonyl and sulphonyl isocyanates with hydrazoic acid under pressure in benzene solution, with cooling, leading to the formation of the azides of *N*-carbonyl- and *N*-sulphonyl-carbamic acids (XXXI) respectively:

$$AcNCO + HN_3 \rightarrow \underset{(XXXI)}{AcNHCON_3},$$

where Ac = RCO or p-$CH_3C_6H_4SO_2$.

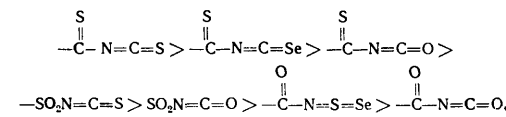
Carbonyl isothiocyanates react relatively smoothly also with dialkylsulphoxides to form *N*-acylsulphilimines [180]:

$$RCONCO + (R')_2SO \rightarrow RCONS(R')_2 + CO_2.$$

In a similar reaction sulphonyl di-isocyanates react with two moles of dimethylsulphoxide to form *NN*-sulphonylbis-(*SS*-dimethylsulphilimine) $(CH_3)_2S{=}N{-}SO_2{-}N{=}S(CH_3)_2$ in 54% yield. Chlorosulphonyl isocyanate gives rise to a 75% yield of *N*-chlorosulphonyl-*SS*-dimethylsulphilimine [196]:

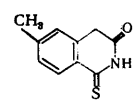
$$ClSO_2NCO + (CH_3)_2SO \rightarrow (CH_3)_2S{=}NSO_2Cl \xrightarrow[HCl]{H_2O} (CH_3)_2S{=}N{-}SO_3OH.$$

In our examination of the chemical properties of acyl isocyanates and isothiocyanates, we frequently mentioned the unequal activities of the latter in various chemical reactions. The data reviewed here make it possible to arrange thio(seleno)acyl and acyl iso(thio, seleno)cyanates in the following series of decreasing activity in various chemical reactions:



VI. APPLICATIONS OF ACYL ISOCYANATES, ISOTHIOCYANATES, AND ISOSELENOCYANATES

Above it was shown that acyl isocyanates, isothiocyanates, and isoselenocyanates are very reactive organic compounds. They enter into a wide variety of chemical reactions, yielding organic products which are valuable for syntheses and for practical applications: urethanes, thiourethanes, urea, thiourea, selenourea, semicarbazides, thiosemicarbazides, and selenosemicarbazides. Various

† 

(Ed. of Translation).

derivatives of heterocyclic compounds have been prepared from them: pyrimidine [101,103,114,117,139,140,143,144,148,149,297], thiazole [111,112,126-128], imidazole [46,116,184], triazole [52,131,166], triazine [52,114,185,188,189], isothiazole [143,144], benzoxazine [145], quinazoline [148], oxathiolane [154], oxazoline [161,163], thiazoline [53,161,163], thiazine [53], thiadiazine [51,53], thiadiazole [170-172], oxadiazine [185-187], isoquinoline [194], and others.

Acyl isocyanates and isothiocyanates have found wide application for the identification of alcohols [88] and amines [98,106] and also for the determination of the structure of nucleic acids and peptides [46,101,103,198]. They are used as copolymers [23,38,199]. Valuable rubbers and fire-resistant polyurethane foam plastics have been obtained on their basis [102].

Acyl isocyanates and isothiocyanates and derivatives based on them exhibit a wide spectrum of biological and chemotherapeutic activity. Compounds with pesticide activity have been found among them [200]. A number of the substances synthesised have been tested as antidiabetic agents [122,124] and depressants of the central nervous system [201].

Many organic substances synthesised using acyl isocyanates and isothiocyanates exhibit considerable antitubercular [202], hypoglycemic [121], anaesthetic [203], anticonvulsant [202,204], and hypnotic [16] activity.

After this review had been submitted for publication, the following papers appeared.

1. On the methods of synthesis of acyl isocyanates [205-210,250-253], acyl isothiocyanates [211,212,251,254], thioacyl isocyanates [85,213,248], sulphinyl isocyanates [214], sulphonyl isocyanates [215-217,255-257], and sulphonyl isothiocyanates [218,220].

2. On chemical reactions with alcohols [221,258-260], mercaptans [222], amines [223-230,261-267], amides [231], hydrazines [232,233,268,269], aziridines [234], compounds containing an active hydrogen atom [235-239,270,271], dienes [240,272-274], Grignard reagents [241], azomethines [242,243,275], chlorine [244,245], nitrosonium salts [246], phosphorus pentasulphide [247], hydrazoic acid [248,276], heterocyclic compounds [248,249], hydroperoxides [277], carboxylic acids [278], and sulphonic acids [279].

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New Data on Biradicals

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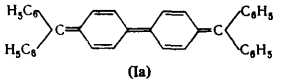
Data on biradicals, including both the results of studies by pre-1947 methods (static magnetic susceptibility, ortho–para conversion of hydrogen, etc.) and the results of studies on biradicals by electron spin resonance are reviewed. Biradicals of various types are discussed—biradicals in the singlet ground state which pass to a triplet state on excitation and biradicals in the triplet ground state which arise in consequence of the degeneracy of higher occupied levels, the presence of an insulating group between the monoradical components, atropisomerism, etc. A complete compilation is also given of all the data on biradicals with heteroatoms. The application of the electron spin resonance method to biradicals permitted an approach to the problems of the interaction of unpaired electrons in these systems. The theory of such interaction and the form of the spectra which should be obtained in its presence and absence are discussed. However, many studies on this interaction have proved erroneous because the data obtained did not refer to the substances to which the observed spectra were attributed but to the products of their further reactions—the formation of di- and poly-mers. These problems are not usually discussed in sufficient detail in physical papers on biradicals, while in the present review special attention has been given to them.

CONTENTS

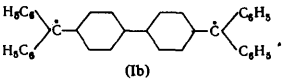
I.	Introduction	376
II.	Biradicals with the singlet ground state	379
III.	Biradicals with insulating groups	381
IV.	Atropisomers	383
V.	Polyradicals	384
VI.	Biradicals with heteroatoms	384
VII.	Biradicals of metal ketyls	389

I. INTRODUCTION

Advances in the modern theory of organic compounds include significant progress in the solution of the problem of biradicals. These are compounds, the molecules of which have, in contrast to monoradicals, an even number of electrons (so structures can be written for them with all electrons paired), but which nevertheless exhibit the properties of radicals, in this case "double" radicals. This term includes substances of three different types. The first includes ordinary molecules with a singlet ground state which can exhibit the properties of radicals because of the possibility of transition to an excited triplet state, so that there is an appreciable concentration of molecules in the triplet state in equilibrium with those in the singlet ground state. Such an approach to biradicals of this type made it possible to resolve the old controversy about whether compounds such as Chichibabin's [frequently spelt Tschitschibabin's (Ed. of Translation)] hydrocarbon have a quinonoid or benzenoid structure:

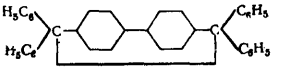


(Ia)

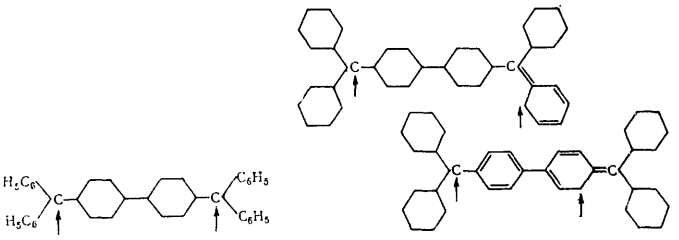


(Ib)

All the structures with the overall spin $S = 0$ (Ia) and others such as, for example,



have been represented in the singlet state, while the triplet state can be described as the superposition of the structures



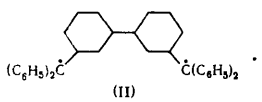
etc. For compounds of this class, the problem consists mainly in the detection of the triplet state and the explanation of the reasons for the relative ease of transition to the latter.

In any molecule with an even number of electrons a transition to the triplet state is possible in principle when the overall spin is equal to unity, i.e. there are two unpaired electrons. However, in the vast majority of organic compounds the excitation to the triplet state requires a very considerable energy and the equilibrium fraction of triplet molecules is low. The substances which exhibit the properties of biradicals are those in which the triplet state is separated from the singlet ground state by a relatively small energy difference. An attempt to account for such relations between the energies of substances of this type was made by Dyatkina and Syrkin [1] on the basis of calculations by the MOH method†. The authors postulated a correlation of the energy difference between the highest occupied and lowest free one-electron levels with the energy of excitation from the singlet to the triplet state. Strictly speaking these quantities cannot be regarded as identical. Calculations of the energy differences between the singlet and triplet states of the molecule as a whole require that the interelectronic repulsion be taken into account. Nevertheless the hypothesis of a parallel variation of the energies of the one-electron transition and the

† MOH—the molecular orbital method in Hückel's approximation.

energy of excitation to the triplet state agrees satisfactorily with the findings that the tendency towards the transition to the biradical state and the fraction of the biradical form in equilibrium clearly increase as the energy of the one-electron transition decreases.

The second type of biradicals constitute substances the molecules of which have a triplet ground state because of the degeneracy of the upper occupied levels, as should happen in cyclobutadiene and *meta*-quinonedimethane and substances such as the hydrocarbon of Schlenk and Brauns (II):



(II)

Cyclobutadiene and *meta*-quinonedimethane themselves have not been obtained. The hydrocarbon of Schlenk and Brauns and its analogues are probably dimers and the possible partial dissociation of such dimers at an elevated temperature does not present a special problem—it is fully included in the problem of the dissociation of dimers of monoradicals such as triphenylmethyl.

The third type of biradicals are molecules consisting of two parts each of which is an ordinary monoradical, but in which the overall molecule is constructed in such a way that the interaction between the unpaired electrons over a distance corresponding to a normal C–C π-bond is impossible because of the presence of an insulating group—for example, an oxygen atom, one or several $-CH_2$ groups, etc. This class includes substances which are formally derivatives of Chichibabin's hydrocarbon (I), but in which the two halves of the molecule are located in planes forming a considerable angle relative to one another due to the steric hindrance of the substituents, and this also prevents the interaction between the electrons of the two halves. With compounds of this type, the central problem is the question whether or not they consist of two completely independent halves, i.e. are in fact two radicals, or whether electron exchange takes place between the two components.

A review of information about biradicals which had accumulated towards the middle of the 1940's was published in 1947 by Dyatkina and Syrkin[2]. At that time the data on the biradical state were based mainly on measurements of static magnetic susceptibility. In some cases such data were confirmed by investigations of the ortho–para conversion of hydrogen.

However, the method of static magnetic susceptibility has considerable limitations. The magnetic susceptibility measured experimentally is the sum of two parts which have different signs: the diamagnetic and paramagnetic susceptibilities. In order to determine the paramagnetic susceptibility, it is necessary to subtract from the total susceptibility the diamagnetic component, which cannot be measured directly. Therefore the diamagnetic susceptibility is calculated from the increments corresponding to individual bonds or atoms. Such a procedure can involve considerable errors. When one deals with strongly paramagnetic substances, their paramagnetism obscures the diamagnetism to a large extent and experiment shows their behaviour to be paramagnetic. This is in fact the behaviour of organic substances when there is a large concentration of radical species, i.e. in the case of biradical molecules in the triplet state in which we are interested. The inaccuracy of the diamagnetic susceptibility may then lead to a small error in the numerical value of the paramagnetic susceptibility but does not prevent, in principle, the detection of radicals and biradicals. On the other hand, if the fraction of biradical species is small, the paramagnetic susceptibility corresponding to them may be extinguished due to the presence of a very large number of diamagnetic molecules. Then the substance behaves as a diamagnetic material, despite the presence of paramagnetic molecules. The fraction of such paramagnetic species, which are not taken into account, may reach 10%. This was in fact the reason for the prolonged controversy concerning the question of the presence of an appreciable fraction of biradical molecules in Chichibabin's hydrocarbon.

Furthermore, in the case of biradicals, apart from the equilibrium between the monomeric singlet and triplet molecules, there is a possibility of thermodynamic equilibrium between paramagnetic monomers on the one hand and diamagnetic dimers (or polymers) on the other. This is an additional complication, which makes it difficult to arrive at a conclusion concerning the concentration of biradicals on the basis of static magnetic susceptibility.

In biradicals there may be different degrees of interaction between the unpaired electrons—ranging from the case where the spins of the two electrons give a resultant spin equal to unity to those where the spins of both unpaired electrons are separated from one another and behave independently. These extreme cases correspond to different values of their magnetic susceptibility. (For $S = 1$, the magnetic moment $\mu = \sqrt{4S(S+1)}\mu_B = \sqrt{8}\mu_B$ and the magnetic susceptibility at 300°K is $N\mu^2/3kT = 3390 \times 10^{-6}$ e.s.u., while in the presence of two separated spins, each of the latter corresponds to a magnetic moment $\mu = \sqrt{3}\mu_B$ and the magnetic susceptibility is 1280×10^{-6} e.s.u., so that the overall susceptibility is 2560×10^{-6} e.s.u.). However, it is impossible to distinguish them on the basis of measurements of the static susceptibility, since systems in which all the molecules are in the biradical state are almost never investigated.

A new stage in the development of our knowledge about biradicals began when the method of electron spin resonance became available. Without changing significantly the basic postulates concerning biradicals, these investigations greatly extended the available information about this interesting class of substances. In the first place, the method makes it possible to establish the presence of biradicals in those cases where data on static magnetic susceptibility do not permit unambiguous conclusions. An even more significant factor is that, with the aid of this method, an approach is possible to the question of the interaction between the unpaired electrons in biradicals.

It is known from ESR theory that, when a conjugated organic system has only one unpaired electron, i.e. we are dealing with a monoradical, the spectrum of such a monoradical in solution can be described by a spin-Hamiltonian of the form

$$\hat{H} = g\beta \mathbf{H}_0 \mathbf{S} + \hat{A}\mathbf{S}\mathbf{I}, \qquad (1)$$

where the first term describes the interaction between the electron spin and the external magnetic field $\mathbf{H}_0$ and the second the hyperfine interaction of the electron spin with the magnetic moment of the nucleus (g is the factor and β a Bohr magneton). In this case the resonance condition can be written thus:

$$h\nu = g\beta H_0, \qquad (2)$$

which corresponds to the allowed transitions $\Delta m_S = +1$, where m_S is a projection of the electron spin. However, in a spin-Hamiltonian system consisting of two unpaired

electrons it is necessary to introduce an additional term describing the interaction between the electron spins:

$$JS_1S_2 ,$$

where J is an exchange integral of the type

$$J = \int \Phi_A(1)\Phi_B(2)\frac{e^2}{r_{12}}\Phi_A(2)\Phi_B(1)\,dv_1dv_2 , \qquad (3)$$

Φ_A the orbital of the unpaired electron in one half of the molecule and Φ_B the orbital in the second half, and r_{12} is the distance between the two electrons.

From the complete formulation of the spin-Hamiltonian in the form

$$\hat{H} = g\beta\mathbf{H}_0(\mathbf{S}_1 + \mathbf{S}_2) + A(\mathbf{S}_1\mathbf{I}_1 + \mathbf{S}_2\mathbf{I}_2) + J\mathbf{S}_1\mathbf{S}_2 \qquad (4)$$

it follows that the hyperfine structure in this case depends not only on the magnetic interaction between the electrons and nuclei but also on the extent of exchange J between the two electrons. If there is no interaction between the electron spins ($J = 0$), resonance will be observed under the same conditions as in a monoradical. If this interaction is sufficiently large and leads to an overall spin $S = 1$, then the transition $\Delta m_S = +2$ also becomes possible. The resonance condition can be written thus:

$$h\nu = 2g\beta H_0 , \qquad (5)$$

which in the presence of a field $0.5H_0$ corresponds to an ESR signal with a formal g-factor of 4.

The changes in the ESR spectra due to the presence of exchange can be best understood as follows. In the presence of exchange interactions between two electrons the energy levels can be described to a certain approximation by the magnetic quantum numbers M_1 and M_2 for the two nuclei, where M_1, $M_2 = -I, -I+1, \ldots, I-1, I$ are the projections of the spins of the nuclei on the z axis and m_1 and m_2 are the projections for the two electrons (m_1, $m_2 = -S, -S+1, \ldots, S$).

If it is assumed that each electron interacts only with its nucleus, the following expression is obtained for the energy:

$$E = g\beta H_0(m_1 + m_2) + A(m_1M_1 + m_2M_2) \qquad (6)$$

or

$$E = g\beta\left(H_0 + \frac{AM_1}{g\beta}\right)m_1 + g\beta\left(H_0 + \frac{AM_2}{g\beta}\right)m_2 . \qquad (7)$$

It is evident from the second equation that the hyperfine interaction for electron 1 is equivalent to a magnetic field $AM_1/g\beta$ set up by the nucleus with a spin I near this electron, while for electron 2 the field is $AM_2/g\beta$. Under the action of a high-frequency field ν applied at right angles to the direction of the permanent magnetic field H_0, resonance transition determined by the selection rules $\Delta m_1 = +1$, $\Delta m_2 = 0$, or $\Delta m_1 = 0$, $\Delta m_2 = 1$ will occur, i.e. the spin of each electron changes by unity. Since an electron transition does not involve changes in the orientation of the nuclear spin, the second selection rule can be written $\Delta M_1 = \Delta M_2 = 0$, i.e. the transitions will occur between states with the same projections of the nuclear spin. In Eqns. (2) and (7), it is possible to determine the resonance values of the magnetic field at which absorption takes place:

$$H_{1,2} = \frac{h\nu}{g\beta} \mp \frac{AM_1}{g\beta} . \qquad (8)-(9)$$

The difference between them is

$$\Delta H = \frac{2AM_1}{g\beta} . \qquad (10)$$

Such a system of equations can also be written for the second electron.

For two nuclei with the same spin values $I_1 = I_2 = I = 1/2$, we have $\Delta H = A/g\beta$, and the line splits into $(2I + 1)$ components, separated by a distance A.

When the exchange between the unpaired electrons is extensive, it can be assumed that the two electrons form a system described by the quantum numbers S and m, where $S = 0,1$ and $m = -S, \ldots, S-1, S$. As before, the nuclei are characterised by the magnetic numbers M_1 and M_2. Then the energy of the system can be expressed in the form[3]

$$E = g\beta H_0 m + \frac{A}{2}(M_1m + M_2m) + \frac{1}{2}J\left[S(S+1) - \frac{3}{2}\right] . \qquad (11)$$

If $g\beta H_0 \ll J$, $g\beta H_0 \gg A$, and $J \gg A$, then the levels of the triplet are of the form $\frac{1}{4}J$ and $\frac{1}{4}J \pm g\beta H_0 \pm \frac{1}{2}AM$, where $M = M_1 + M_2$. Taking into account the selection rules $\Delta m = +1$ and $\Delta M = 0$, we obtain an electron transition at $h\nu = g\beta H_0$ with $2M + 1$ hyperfine components. The distances between them are $A/2$ and not A as was the case for two independent electrons.

Apart from the $h\nu = g\beta H_0$ transition allowed by the selection rule $\Delta m = +1$, the interaction between the electrons also leads to partial absorption of the field energy on transitions between levels with spin projections $m_S = 1$ and $m_S = -1$ ($\Delta m = \pm 2$). It is evident from Eqn. (5) that this transition corresponds to a g-factor twice as large as for the free electron, i.e. here the g-factor should be approximately 4.

The derivation of expressions for the frequency of transitions and their probabilities in a general form on the basis of Eqn. (4) is a very complex problem, which has been solved only for certain special cases. Sakun et al.[4] describe the motion of unpaired electrons by an effective self-consistent potential, which for a biradical has the form of a well with two minima. Then calculation leads to an ESR spectrum consisting of three frequency groups:

$$\omega_{1,2} = A(M_1 + M_2) \pm 2\sqrt{J^2 + [(A/2)(M_1 - M_2)]^2} , \qquad (12)-(13)$$

$$\omega_3 = A(M_1 + M_2) . \qquad (14)$$

Taking into account the selection rules specified above, the intensities of the corresponding lines are

$$F_{\omega_{1,2}} = \frac{1}{1 + (J/A)^2\left(\frac{2}{M_1 - M_2}\right)^2} , \qquad (15)$$

$$F_{\omega_3} = \frac{2}{1 + (A/J)^2\left(\frac{M_1 - M_2}{2}\right)^2} . \qquad (16)$$

It follows from these formulae that, when $J = 0$, there are no ω_3 frequencies in the ESR spectrum, and there remain $(2I_{1,2} + 1)$ lines of equal intensity. In the case of rapid exchange ($J \gg A$) there are no lines corresponding to the frequencies ω_1 and ω_2 and there remain $4I + 1$ lines with the intensities $1:2:3:2I:2I+1\ldots 3:2:1$. In the intermediate cases there are only $(2I + 1)^2 + 2$ lines. Fig. 1 shows that, for two electrons located respectively at two nuclei with a spin $I = 1/2$, the number of lines ranges from 2 in the absence of exchange $[(2I + 1) = 2]$ to 3 $[(4I + 1) = 3]$ when the extent of exchange greatly exceeds the hyperfine interaction constant. With intermediate values of J, "satellite" lines, characteristic of biradicals, appear at the wings of the relevant absorption curve and between the principal lines.

Thus the value of the g-factor for those cases where there are $\Delta m = +2$ transitions, and also the number of hyperfine components and their intensities, which both

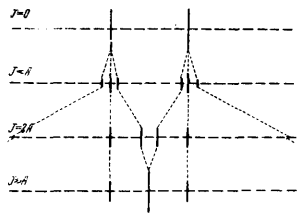


Figure 1. Theoretical spectrum for two electrons and two nuclei with a spin of 1/2.

depend on J, provide information about the degree of electron interaction in biradicals.

The aim of the present review is to examine the data on biradicals obtained with the aid of the ESR method. Furthermore, additional data on the chemical and physical properties of biradicals which have appeared in the literature since the 1947 review will be included. Molecules belonging to all three types of biradicals considered above will be discussed.

II. BIRADICALS WITH THE SINGLET GROUND STATE

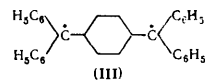
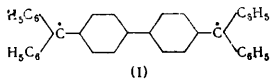
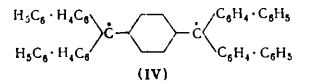
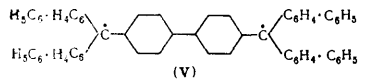
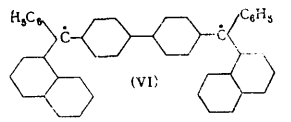
When the ESR method appeared, the biradical nature of compounds could be established, among substances of this type, for which earlier results did not lead to unambiguous conclusions. This applies in the first place to the forerunner of such substances, namely Chichibabin's hydrocarbon, for which both the static susceptibility and the ortho–para conversion of hydrogen methods failed to solve the problem of whether the substance passes to a biradical state under normal conditions. In his measurements of the static magnetic susceptibility, Müller[5] observed diamagnetism and on this basis rejected the possibility of the presence of molecules in the triplet state. However, the work of Schwab and coworkers[6], who investigated the ortho–para conversion of hydrogen in the presence of Chichibabin's hydrocarbon, indicates the presence of a considerable fraction (up to 10%) of biradical molecules.

Even the first investigations of this compound by the ESR method, carried out by Hutchinson et al.[7], showed that 0.005 M liquid solution contains 4% of paramagnetic molecules and that this fraction can increase with temperature.

It should be noted that fully reproducible results are not always achieved in the synthesis of substances of the Chichibabin's hydrocarbon type. Some workers obtained very brightly coloured solutions and assumed that the reaction products are biradicals in the monomeric state. Others obtained colourless substances consisting in all probability of dimers or polymers. It was not until 1957 that Sloan and Vaughan[8] developed the most complete modern method for complex syntheses of biradicals[8]. They obtained a number of derivatives of Chichibabin's hydrocarbon showing as distinct a resonance paramagnetic absorption as in hydrocarbon (I)—the parent of this type of compounds (Table 1).

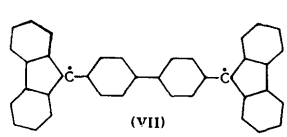
On the other hand Thiele's hydrocarbon(III) does not give rise to an ESR signal since the fraction of molecules in the triplet state is extremely low, but the tetra(biphenylyl) derivative (V) does exhibit resonance absorption. These data are in good agreement with the results of the calculations of the energies of the highest occupied and lowest free orbitals by the MOH method. In Thiele's hydrocarbon the energy of this transition (0.31β) is greater by a factor of 2 than in Chichibabin's hydrocarbon (0.15β). This explains why an appreciable fraction of biradical molecules is observed in the first compound, while in the second it is much smaller. The introduction into Thiele's hydrocarbon of biphenylyl groups [compound(IV)] instead of phenyl groups also reduces the energies of the highest occupied and lowest free orbitals (to 0.13β), which leads to a concentration of molecules in the triplet state susceptible to detection.

Table 1.

Compound	Presence of ESR signal	Colour of solution
 (III)	—	orange
 (I)	+	violet
 (IV)	+	brick red
 (V)	+	bright blue
 (VI)	+	dark purple

It is noteworthy that all these substances readily undergo changes in which the radical properties are probably lost. When air is admitted, only compound (III) and compound (IV) do not change colour, while compounds (I), (V), and (VI) are decolourised. This shows that conclusions concerning the biradical character of a substance can be arrived at only in those cases where special precautions have been taken to prevent dimerisation and polymerisation, oxidation, decomposition, etc.

A new compound of this class synthesised by Theilacker et al.[9] is 4,4'-bis(9-fluorenyl)biphenyl (VII):



(VII)

It proved to be a colourless sparingly soluble polymer. When a solution in α-methylnaphthane was heated from 80° to 165°C, its colour changed from brown to bright green. Depolymerisation with increase of temperature is accompanied by an appreciable increase in paramagnetism, possibly in consequence of dissociation into monomeric biradicals (Table 2).

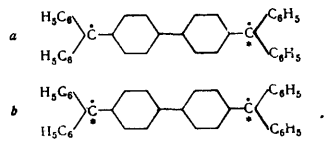
The first investigations of biradicals, where only the presence or absence of paramagnetism in the given molecules was established, were followed by the study of the intramolecular interactions between the two unpaired electrons. For substances of the type of Chichibabin's hydrocarbon, which have a singlet ground state, this problem has no physical significance. In the triplet state of these molecules, as in the triplet states of any other normal molecules, there are no separate components where unpaired electrons could be localised. The problem of whether or not there is interaction between two halves,

Table 2.

Temperature, °C	$\chi_{exp}-\chi_{calc}$	biradical content, %
20	—	—
105	+45	3
145	+141	8
165	+153	9

constituting in fact a single conjugated system, arose only due to the traditional approach whereby the structure of the triplet form of Chichibabin's hydrocarbon was represented as consisting of two triphenylmethyl radicals joined by a C–C bond in the *para*-position. However, it is possible to demonstrate by this example the errors which can arise in studies of ESR spectra without due attention being given to a reliable identification of the compounds to which the spectra refer. We shall consider the relevant studies because they demonstrate the danger of theorising about unusual properties of molecules in those cases where there is no certainty that they are in fact the properties of the molecules under consideration and not of some others (for example conversion products), for which they are reasonable and by no means surprising.

In an early investigation[10] it was found that the g-factors of Chichibabin's hydrocarbon and its diphenyl and phenylnaphthyl derivatives [compounds (V) and (VI)] are 2.0025 ± 0.0004, although transitions corresponding to $\Delta m = +2$ might also have been expected. The spectra were poorly resolved so it was difficult to draw inferences concerning the number of hyperfine structure lines. Later Reitz and Weissman[11] investigated the electron spin resonance of Chichibabin's hydrocarbon where the carbon atoms marked with an asterisk were labelled with carbon-13, the atomic nucleus of which itself has a magnetic moment. One atom was labelled in case *a* and both atoms in case *b*:



For system *a* ($^{12}C-^{13}C$), where there is only slow exchange compared with the frequency of hyperfine interaction, i.e. $A \gg J$, a triplet spectrum should have been obtained with a central line originating from the part of the molecule where the nuclear spin is zero, i.e. from the $(C_6H_5)_3{}^{12}C$ group, and two outer lines with intensities smaller by a factor of 2, which are due to splitting by carbon-13 in the $(C_6H_5)_3{}^{13}C$ group (Fig. 2).

The spectrum of system *b* ($^{13}C-^{13}C$) should consist of two lines in the presence of slow exchange (each electron located at its nucleus and $A \gg J$) or three lines with intensities 1 : 2 : 1 in the presence of rapid exchange, when the spins migrate from one half of the molecule to the other (Fig. 1).

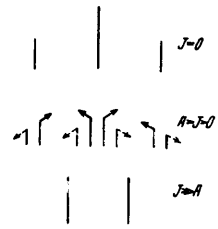


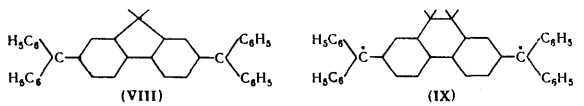
Figure 2. Theoretical spectrum of Chichibabin's hydrocarbon with a single ^{13}C tracer atom.

A surprising result of this investigation was the finding that the experimental data can be interpreted as demonstrating that the structure of the molecule of Chichibabin's hydrocarbon consists of two independent triphenylmethyl components with a frequency of exchange between the latter $< 7 \times 10^7$ s^{-1}, which was completely incomprehensible when the radical form of Chichibabin's hydrocarbon was treated as a triplet state of the molecule. However, instead of thoroughly testing the reliability of the experimental data and in the first place identifying the molecules which give rise to the spectra, a number of investigators undertook the development of a "theory" of these fantastic phenomena.

McConnell[12] estimated theoretically the frequency of hyperfine splitting on the basis of the singlet–triplet splitting Δ in the biradical, adopting for Δ the value found in the calculation by the simple MOH method, and obtained an exchange frequency of the order of 2.5×10^{13} s^{-1}. This discrepancy with the "experimental" value ($< 7 \times 10^7$ s^{-1}) led to the so called "biradical paradox", to the resolution of which a number of studies were devoted[12–14]. McConnell in fact started from the premise that Δ is determined only by the frequency of transmission of an electron from one half of the molecule to the other. Burshtein and Naberukhin[15] attempted to obtain a closer agreement between the theoretical estimate of the frequency of electron exchange and the "experimental" value by considering the mutual electrostatic repulsion of the electrons, i.e. by going over to the two-electron problem. When account is taken of the Coulombic interaction, singlet–triplet splitting is obtained corresponding to an exchange frequency of the order of 10^6 s^{-1}, i.e. a value close to or somewhat smaller than the frequency of hyperfine interaction. An impression was created that Chichibabin's hydrocarbon can indeed be regarded as consisting of two halves. However, the inconsistency of this conclusion with the general hypotheses concerning the origin of the biradical nature of substances of this type led to further studies in this field.

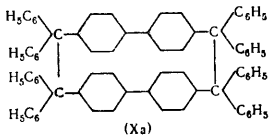
The latest results obtained by Waring and Sloan[16] provide a new interpretation of the observed independence of the unpaired electrons in Chichibabin's hydrocarbon: it is now attributed to a biradical dimer and not to the individual

monomeric molecule of the biradical. When, in experiments on Chichibabin's hydrocarbon and the biradicals (VIII) and (IX),



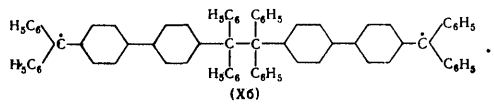
(VIII) (IX)

the specimen is cooled sufficiently rapidly, the intensity of the ESR spectrum observed at room temperature persists also at the low temperature. This can be regarded as proof that at sufficiently low temperatures the solution does not contain only monomeric biradicals but there is an equilibrium between paramagnetic and diamagnetic molecules. The most likely type of association is due to the formation of a weak C–C bond, as in hexaphenylethane. This may give rise to the formation of both diamagnetic cyclic dimers of the type



(Xa)

and linear dimers (or polymers) which retain a biradical character:



(Xб)

The linear dependence of the intensity of the ESR signal on concentration in the range between 5.04×10^{-3} and 7.7×10^{-5} M at room temperature (Fig. 3) shows that the associated paramagnetic and diamagnetic molecules have the same molecular weight.

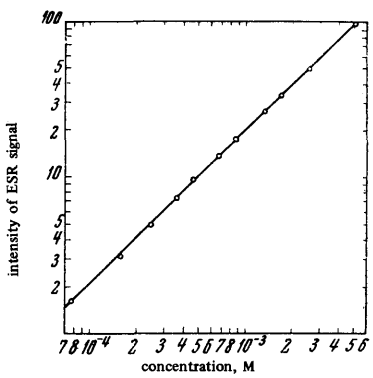


Figure 3. Variation of signal intensity with the concentration of Chichibabin's hydrocarbon in carbon disulphide.

The ESR spectrum of the biradical (VIII) at 25°C is shown in Fig. 4; the intensities of the lines in an individual section of the complete spectrum persist also on heating to 100°C, i.e. under these conditions there are no changes associated with the interaction between the electrons.

The presence of dimers or polymers of type (Xa) and (Xb) inevitably leads to observed independence of the unpaired electrons. These results provide a clear illustration of the danger of investigating exchange interactions on

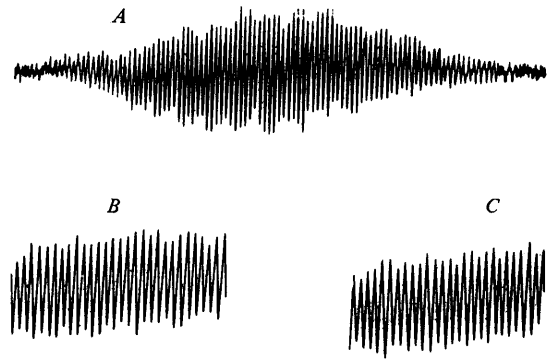
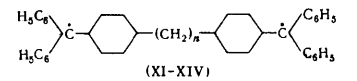


Figure 4. ESR spectrum of the biradical (VIII) in carbon disulphide: *A*) complete spectrum at 25°C; *B*) section of the spectrum at 25°C; *C*) section of the spectrum on heating to 100°C.

the basis of ESR spectra without a detailed identification of the molecules to which these spectra refer. Thus, the ESR data in no way contradicted the treatment of compounds of the type of Chichibabin's hydrocarbons as normal molecules with a low energy of excitation to the triplet state.

III. BIRADICALS WITH INSULATING GROUPS

Bridged biradicals [(IX)–(XII)], among which diphenylmethane and diphenylethane may be included, were obtained for the first time by Wittig and Leo[17,18].

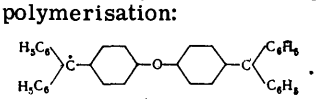


(XI-XIV)

(n = 1,2,3,4).

From the chemical point of view, they behave as free radicals; compound (XI) formed a bright red and compound (XII) a dark red solution exhibiting green dichroism in thin layers. However, in diphenylbutane derivatives (XIV) radical properties were completely absent according to the results of Wittig and Leo[18]. They attributed the weak colour, slow reaction with oxygen, and the constancy of the colour of this hydrocarbon to disproportionation. Nevertheless latest work[19] has shown that solutions of triarylmethyls frequently retain the initial colour although their paramagnetism falls to zero. All this weakens the arguments of Wittig and Leo.

Measurements of static magnetic susceptibility[20] led to the conclusion that hydrocarbon (XII) is diamagnetic; Müller failed to repeat the Wittig synthesis and his compound was completely colourless. Compound (XV), synthesised by Müller and Bunge[21], also proved to be diamagnetic (according to measurements of static magnetic susceptibility) and its diamagnetism was explained by dimerisation or polymerisation:



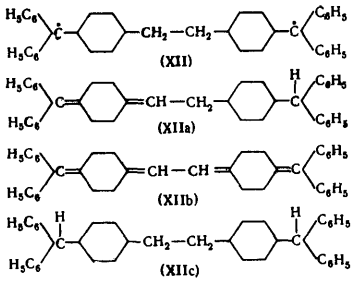
(XV)

The biradicals (XI)–(XV) have now been studied by the ESR method[10,11]. Table 3 shows that they exhibit intense paramagnetic absorption, but even in the absence of light and oxygen the paramagnetism vanishes after a time. This is evidently due to disproportionation. In his study of the

Table 3.

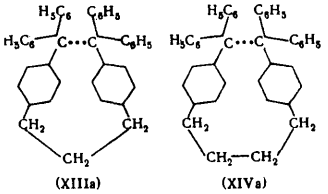
Compound	Initial colour	Presence of ESR signal	Colour of decomposed solution	Colour after access of air
(XI)	bright red	++	pale yellow	colourless
(XII)	wine red (green in thin layers)	++	pale blue	colourless
(XIII)	yellow	++	pale yellow	pale yellow
(XIV)	yellow	++	pale yellow	pale yellow
(XV)	yellow	++	pale yellow	pale yellow

biradical (XII), Müller obtained three decomposition products which he believed appeared as a result of subsequent inter- and intra-molecular disproportionation reactions.



It is interesting to note that, although compound (XIIb) is diamagnetic, it has a dark red colour and is sensitive to oxygen. Judging from Tables 1 and 3 compiled by Sloan and Vaughan[8], conversion into coloured diamagnetic compounds which retain their sensitivity to oxygen is a common property of biradicals.

Speaking of the disproportionation mechanism, it is difficult to explain why the colour of the decomposed solution of compound (XI) differs from that of the solution of compound (XII), if it is assumed that inter- and intramolecular disproportionation converts compound (XI) to the same product. Furthermore, it is not altogether clear why diphenylpropane and diphenylbutane differ so much from diphenylmethane and diphenylethane derivatives. Possibly the biradicals forms (XIII) and (XIV) are in equilibrium with monomeric diamagnetic compounds of the type (XIIIa) and (XIVa), since in compounds (XI) and (XII) intramolecular saturation of valence is impossible, because the bond between trivalent carbon atoms would have to extend over a very large distance. This difference in fact leads to different disproportionation mechanisms:



The central problem which arises in the examination of biradicals with insulating groups is the question whether the biradical in fact consists of two independent monomeric radicals or whether there is exchange interaction between the two halves, leading to a spin $S = 1$. The method of static magnetic susceptibility, which predicted a diamagnetic behaviour of the majority of these hydrocarbons, could not of course resolve this problem.

Analysis of the ESR spectra of bridged biradicals[10] (Fig. 5) favours the first hypothesis, namely that the two halves of the biradical are independent. The measured values of the g-factor proved to be similar to those of a free electron and the sharp resolution of the spectrum and the narrowness of the hyperfine components suggested the absence of appreciable dipole interaction between the unpaired electrons. The impairment of the resolution of the hyperfine structure on increasing the number of methylene groups favours the hypothesis that, with a longer molecular chain, anisotropic hyperfine interaction makes a contribution to line width. The line in the spectrum of compound (XV) again becomes sharp and the g-factor decreases somewhat (from 2.0025 to 2.0031), which is characteristic of free radicals with oxygen atoms[11,12] (Fig. 6).

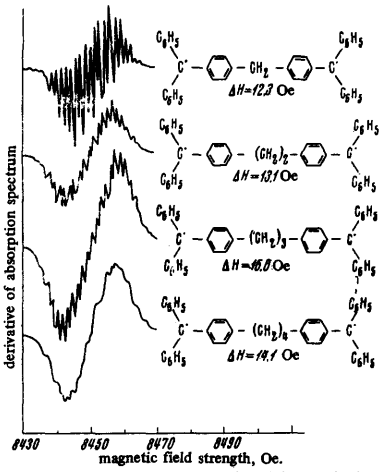


Figure 5. ESR spectra of biradicals with insulating groups.

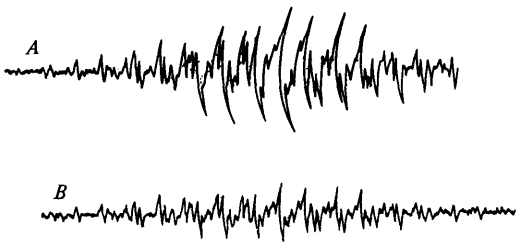
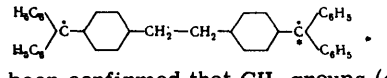


Figure 6. *A*) ESR spectrum of the biradical (XV) at 263°K; *B*) at 215°K.

Analysis of the hyperfine structure in the spectra of biradicals (XII) and (XV) labelled with the carbon-13 isotope, similar to that discussed above, confirmed the independence of the spins of the unpaired electrons[11]. Thus at 297°K the spectrum of compound (XII), in which one of the atoms (marked with an asterisk) was labelled with carbon-13, contains a central line which originates from the part of the molecule in which the nuclear spin is zero. The two outer lines are due to splitting by carbon-13 in the group $(C_6H_5)_3{}^{13}C$. Such a triplet spectrum corresponds to the condition $J = 0$ (see Figs. 2 and 7):



Thus it has been confirmed that CH_2 groups (even one such group) clearly insulate two conjugated systems. It

has been suggested that conjugation via such groups is possible in the radical-anions (monoradicals) of diphenylmethane and dibenzyl[23,24]. However, this has been disproved by the work of Kazokova, Syrkin, and Shapiro, who

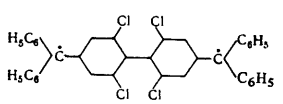
Figure 7. ESR spectrum of the biradical (XII) at 297°K (60% ^{13}C).

showed that the radical-anions are not in this case unchanged initial molecules to which an electron has been added, but undergo secondary reactions, which lead to a considerable rearrangement of the initial molecules[25-27].

IV. ATROPISOMERS

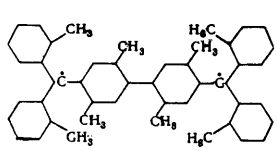
Numerous new data on static magnetic susceptibility were obtained in the 1950's for non-planar derivatives of diphenylquinonedimethane–atropisomers. The presence of bulky substituents in the *ortho*-position with respect to the central bond leads to the rotation of one part of the molecule relative to the other and both halves become just as independent as the bridged biradicals. Therefore, although formally these substances appear to be derivatives of compounds of type 1, in fact they belong to the third type.

The compound 2,6-2′,6′-tetrachloro-4,4′bis(diphenylmethyl)biphenyl (XVI), which in solution exhibits paramagnetism increasing with temperature and decreasing with concentration, was examined earlier by the method of static magnetic susceptibility[28]. Comparatively recently these data were confirmed by the study of the ortho–para conversion of hydrogen catalysed by compound (XVI).[29] It was found that this compound is a biradical to the extent of 100%:

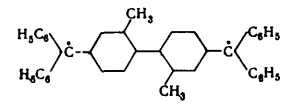


(XVI)

According to the results of Schwab and Baumel[30], compound (XVII) catalyses the ortho–para conversion of hydrogen with a conversion constant likewise corresponding to a 100% content of the biradical. Static magnetic measurements[9] fully confirm the data of Schwab and Baumel concerning the biradical nature of compound (XVII) (Table 4).



At one time Theilacker and Ozegowski[31] suggested that not four but two substituents are sufficient for the breakdown of coplanarity. They synthesised compound (XVIII), Theilacker's hydrocarbon, the solution of which is very sensitive to air and exhibits green-red dichroism. On this basis they suggested that the solution contained the biradical form (XVIII):



(XVIII)

It was not until much later that data on the percentage content of the biradical (XVIII) were obtained by measurements of the magnetic susceptibility of this hydrocarbon in α-methylnaphthalene[9] (Table 5).

Table 4. Magnetic susceptibility of 2,2′,5,5′-tetramethyl-4,4-bis(ditolylmethyl)biphenyl in α-methylnaphthalene (M) and benzene (B).

Concn.%	Temp., °C	$\chi_{exp}-\chi_{calc}$	biradical content, %	Concn., %	Temp., °C	$\chi_{exp}-\chi_{calc}$	biradical content, %
M, 1.5	20	+2493	97		80	+2142	100
	50	+1809	96		99	+1972	98
	80	+2141	100	B, 4.0	20	+2518	99
	105	+1948	98		51	+2329	100
M, 4.6	20	+2494	97		82	+2119	100

Table 5.

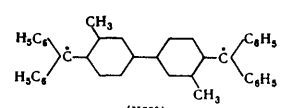
Concentration, %	Percentage of biradical form		
	20°	51°	82°
5.12	4	10	21
4.96	4	8	19
5.05	5	10	21
2.05	5	12	25
2.07	5	12	28

Table 6. 2,2′-Difluoro-4,4′-bis(diphenylmethyl)biphenyl in α-methylnaphthalene.

Concentration, %	Percentage content of biradical form				
	21°	53°	80°	105°	130°
5.00	1	—	8	11	2
5.33	3	—	12	13	11
5.11	2	—	9	13	11
2.62	3	4	9	—	—

The substitution of methyl groups by fluorine atoms leads to a smaller percentage content of the biradical and therefore the equilibrium quinonedimethane ⇌ biradical is more strongly displaced to the left (Table 6).[9]

However, the steric effect is evidently not the only factor in such cases, since substance (XIX), with methyl groups in *meta*-positions with respect to the central bond, is also paramagnetic and actually more so than Theilacker's hydrocarbon[9,32] (see data in Table 7):



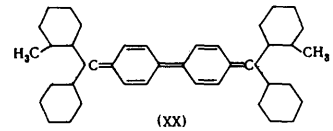
(XIX)

Apart from steric effects, the presence of substituents in the biphenyl system which reduce the energy of excitation to the triplet biradical state probably also plays a significant role in this case.

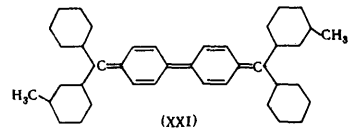
Table 7. 3,3′-Dimethyl-4,4′-bis(diphenylmethyl)biphenyl in α-methylnaphthalene.

Concentration, %	Percentage content of biradical form		
	21°	55°	84°
5.05	14	31	47
4.18	15	32	47
2.23	17	39	50
2.01	18	38	46

Compounds (XX) and (XXI) proved to be diamagnetic[32]:



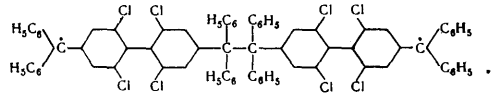
(XX)



(XXI)

It should be noted that data on the percentage content of the biradical forms in atropisomers listed in the tables were obtained on the assumption that both halves of the biradicals are completely independent ($\chi_p = 2560 \times 10^{-6}$ e.s.u.). However, in some cases the angles between the two halves of the biradical can assume intermediate values between 0° and 90°C, which should result in a weak π-bond. Therefore complete reliance cannot be placed on data obtained on the assumption that such a bond is altogether absent.

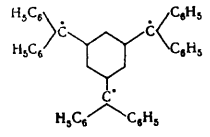
The extent of interaction between unpaired electrons might be inferred from ESR spectroscopic data, but unfortunately the only biradical [compound (XVI)] investigated by this method is appreciably associated in solution[16], forming open-chain biradical dimers (or polymers) of the type



Clearly such association prevents the correct interpretation of the ESR spectra.

V. POLYRADICALS

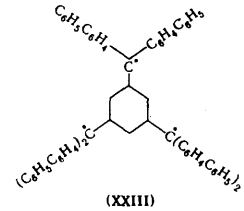
In 1965 there appeared a brief communication that German investigators[33] had succeeded in repeating Leo's attempt to obtain a hydrocarbon triradical of the type



(XXII)

However, the product did not have a definite melting point and, according to elemental analysis and molecular weight measurements, was a weakly associated polymer. On dissolution in benzene, an ESR spectrum with a resolved hyperfine structure appeared.

The replacement of phenyl groups by biphenylyl groups yields the triradical (XXIII)



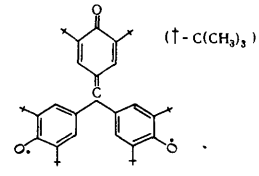
(XXIII)

which consists of red-violet crystals. It gives rise to an ESR signal but the hyperfine structure is not resolved in the spectra of either the solid radical or its solution in benzene. The solution also contains both monomeric and polymeric molecules.

VI. BIRADICALS WITH HETEROATOMS

Recently an intensive study of biradicals with heteroatoms by the ESR method was begun. With the exception of the previously known porphyrindine, most of the radicals constitute completely new classes of paramagnetic organic molecules. As with hydrocarbon biradicals, this method makes it possible to determine from the number of hyperfine components of the ESR spectrum and the g-factor the class of biradicals to which the given compound belongs, i.e. to elucidate whether it is simply a double monoradical or whether it is in the triplet state, like Chichibabin's hydrocarbon.

Jang and Castro[34] described the synthesis of a substance with the hypothetical structure (XXIV)



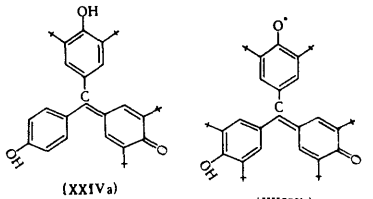
(XXIV)

Calculations were made on this molecule[35] by the MOH method on the assumption that the phenyl rings are displaced from a single plane and are rotated by 30°, as in triphenylmethyl. The calculation led to the conclusion that the last two electrons should occupy a degenerate nonbonding orbital when all the Coulombic integrals are equal, and a degenerate orbital with the energy 0.542β when the Coulombic integral for the oxygen atom is assumed to be $\alpha_O = \alpha_C + 1.5\beta$, so that in both cases there is a triplet ground state. The most significant results proved to be the theoretical prediction of a transition at very long wavelengths (20.000 Å) and its experimental observation in absorption spectra. This transition takes place from the bonding level with the energy 0.827β to the partially filled degenerate bonding levels (0.542β) where the unpaired electrons of the molecule are located.

Measurements of the static magnetic susceptibility gave 3.1×10^{-3} cm³ mole⁻¹ as the paramagnetic contribution. However, in the authors' view there is a possibility here of a large experimental error.

The ESR spectrum of Jang's biradical consists of seven overlapping lines (hyperfine constant $A_H = 0.86$ Oe), which indicates the interaction of the unpaired electrons with six equivalent protons[36]. Evidently the spin exchange is very rapid and each electron interacts with the six *meta*-protons

of the three aromatic rings. The addition to the biradical of the initial substance (XXIVa) in methyltetrahydrofuran leads to the formation of the monoradical (XXIVb):



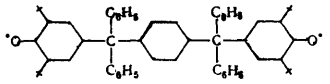
(XXIVa) (XXIVb)

Evidently a disproportionation reaction takes place:

XXIV + XXIVa ⇆ XXIVb.

On cooling a solution containing the biradical, the lines in the ESR spectrum broaden and at −50°C the spectrum consists of a single broad line. In the spectrum of the frozen solution (glass at −160°C) dipole splitting is observed, and the lines originating from the monoradical and the biradical become superimposed (large doublet splitting). The extent of this splitting depends on the dipole interaction between the unpaired electrons, which is inversely proportional to the cube of the distance between the magnetic dipoles. Thus the distance between the intense lines of the doublet enables (see Pake[37]) the distance between the two unpaired spins to be found, in this case 9 Å.

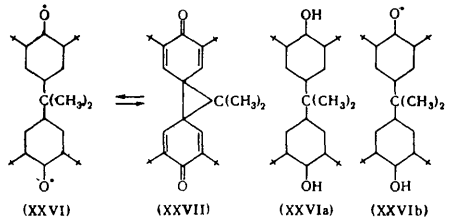
Another bisaroxyl biradical (XXV) was studied by Müller and coworkers[38]. Measurements of static magnetic susceptibility in benzene showed that the solution contained 88% of the biradical molecules. The ESR spectrum of this biradical consists of three lines, which can be attributed to two protons of the phenoxyl ring. Hence it follows that the unpaired electrons are localised only in the phenoxyl groups surrounding the molecule and do not interact with one another via the insulating $C(C_6H_5)_2$ groups, the biradical behaving simply as a double monoradical:



(XXV)

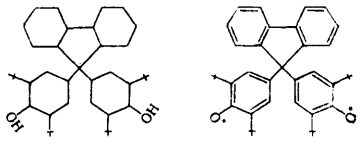
The attempt of Chandross and Kreilick[39] to detect by the ESR method the biradical (XXVI) obtained by the oxidation of compound (XXVIa) was unsuccessful, although the monoradical (XXVIb) gave rise to a distinct ESR spectrum consisting of a triplet (two equivalent *meta*-protons with a hyperfine structure constant of 1.67 Oe) split by the weaker interaction with the six equivalent protons of the isopropylidene group (hyperfine structure constant of 0.38 Oe).

The absence of an ESR signal due to the biradical (XXVI) can be attributed to the equilibrium between the biradical species and the diamagnetic spirodiene (XXVII):



(XXVI) (XXVII) (XXVIa) (XXVIb)

The replacement of the *gem*-dimethyl group in compound (XXVIa) by a 2,2-diphenylene group yields compound (XXVIIIa)[40]. The ESR spectrum obtaining during the oxidation of this substance was investigated. Initially three lines due to the monoradical appeared (hyperfine structure constant of 1.65 Oe). As the oxidation progressed, the intensity of the signal increased and then fell, but did not disappear altogether. At −180°C two groups of lines appeared in the spectrum, corresponding to the transition $|\Delta m| = 1$ with splittings of 126 and 30 Oe, and absorption corresponding to $|\Delta m| = 2$ occurred when the field strength was reduced to 50%. The larger splitting was attributed to the biradical (XXVIII) and the smaller to the dimer containing two molecules of compound (XXVIII), probably joined by a peroxide bond:

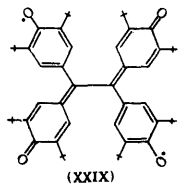


(XXVIIIa) (XXVIII)

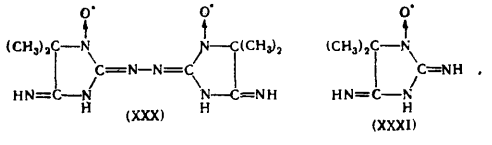
Although the formation of such a bond is fairly unusual in this case (due to the presence of bulky substituents in the phenyl ring), the concentration dependence of the extent of splitting in a zero field confirms the occurrence of dimerisation. On dissolution, the intensity of the smaller splitting decreases and vanishes much faster than that of the larger splitting, which persists for a fairly long time. The position of the lines indicates that the average distance between the unpaired electrons in compound (XXVIII) is 6 Å and in the dimer 9.8 Å.

Recently Chandross[41] obtained an interesting stable biradical (XXIX) which he called bisgalvinoxyl. It is a dark crystalline substance with a metallic lustre. In the solid state the biradical is very stable, but in inert solvents (10^{-3}–10^{-4} M) it is decolourised by air in several hours. The bisgalvinoxyl spectrum recorded in glasses at 77°K clearly shows that this substance is in the triplet state. In methyltetrahydrofuran a hyperfine line structure appears, transitions both from $|\Delta m| = 1$ and transitions at 1635 Oe, corresponding to $|\Delta m| = 2$, being observed. Using the model of 2 point dipoles, it can be shown that the splitting at $|\Delta m| = 1$ corresponds to an average interelectron distance of 6 Å.

In contrast to the biradicals (XXIV) and (XXIX), the ESR spectra of which indicate that these compounds have two unpaired electrons in different parts of the molecule interacting with one another, in the ESR spectrum of porphyrindine (XXX) there is no clear proof of the interaction between the two unpaired electrons[42].



(XXIX)



(XXX) (XXXI)

The spectrum of the dimethylsulphoxide solution of this substance consists of three groups of lines with a hyperfine structure constant of about 10 Oe. Each line is split further into four components with a hyperfine structure constant of the order of 3 Oe (Fig. 8). The main splitting is evidently due to the interaction of the unpaired electron with the nucleus of the nitrogen atom. In contrast to this,

the spectrum of compound (XXX) in ethanol at 300°K consists of only two lines, although porphyrexide (XXXI), which constitutes as it were one half of porphyrindine, gives rise under these conditions to an ESR spectrum consisting of three lines. Possibly in this case there are solvent and temperature effects on the exchange interaction.

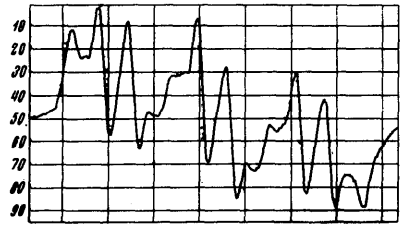
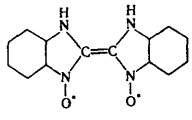


Figure 8. ESR spectrum of the biradical (XXX) in dimethylsulphoxide at 80°C.

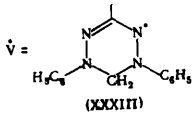
The decrease of the paramagnetism of porphyrindine on reducing the temperature previously, observed by the magnetic susceptibility method, is found to occur also for NO-indigo[43]:



(XXXII)

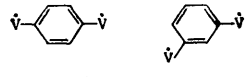
At room temperature the fraction of biradical molecules is high and the susceptibility of this compound is 10% higher than the value calculated for the double monoradical. However, at the temperature of liquid nitrogen it is diamagnetic. Evidently, in this case the diamagnetic form of NO-indigo, like the diamagnetism of porphyrindine at low temperatures, is associated with the displacement of the equilibrium between the diamagnetic and paramagnetic forms towards the former. The diamagnetic form may be either a polymer or, what is more likely, a diamagnetic monomer.

On the basis of the fragment



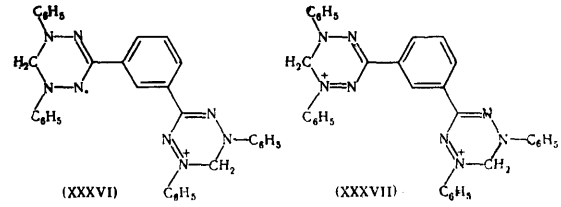
(XXXIII)

the green biradicals (XXXIV) and (XXXV) were obtained[44]:



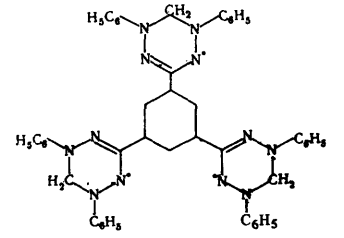
(XXXIV) (XXXV)

While the monomeric radical (XXXIII) gives rise to nine lines in the ESR spectrum, which can be accounted for by interaction with two nitrogen atoms, the spectra of biradicals (XXXIV) and (XXXV) contain a different number of lines, corresponding to exchange between two unpaired electrons. Reversible polarographic oxidation leads to the monocation (XXVI), violet in colour, the spectrum of which again shows the nine lines of the monoradical, and then the diamagnetic dication (XXXVII):



(XXXVI) (XXXVII)

The interesting triradical (XXXVIII) was also obtained on the basis of (XXXIII):[45]

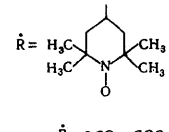


The resultant magnetic spin moment of the molecule for three independent unpaired electrons is $\mu = \sqrt{9}\mu_B$. Table 8 shows that, in contrast to porphyrindine and NO-indigo, the paramagnetism of the triradical does not continue to decrease down to the temperature of liquid nitrogen. This suggests that the three electrons of the triradical are indeed independent. The hyperfine structure of the ESR spectrum of the triradical is unresolved.

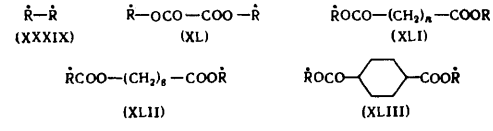
Table 8.

T°K	μ/μ_B
298	2.96+0.06
195	2.97
77	3.01

Because of the presence of an insulating grouping between the two halves of the molecules of the hydrocarbon biradicals examined above, there is no exchange between them, i.e. the σ-bond system of the bridge prevents interaction between the electrons. The insulating bridge in biradicals with heteroatoms plays the same role. However, it has been suggested that the exchange of unpaired electrons can occur also in the presence of insulating groupings, but by a different mechanism. Roxantsev, Buchachenko, and coworkers[46,49] and also Lemair and coworkers[50,51] obtained and investigated iminoxy-biradicals, which are exceptionally stable both in the solid state and in solutions. The iminoxy-biradicals contain the following residue with the unpaired electron:

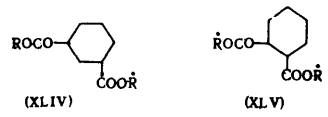


$n = 2, 4, 5$



(XXXIX) (XL) (XLI)

(XLII) (XLIII)



In the absence of exchange between the unpaired electrons in the two halves of the iminoxy-biradical, each electron interacts with the nucleus of the nitrogen atom of "its half" and the biradical behaves as a double monoradical. In this case the ESR spectrum consists of three lines with a hyperfine structure constant A. If there is strong exchange interaction between the two electrons, the spectrum consists of five lines with a hyperfine structure constant $A/2$ (see p. 378 and Fig. 9).

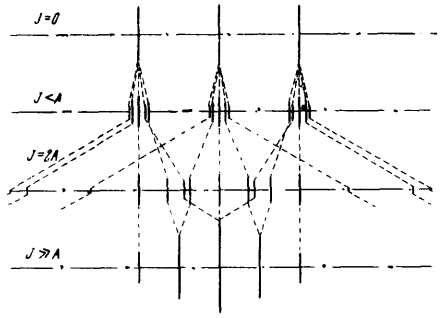
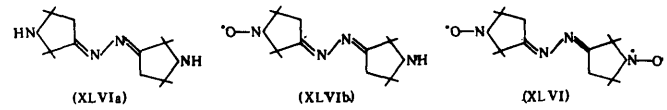


Figure 9. Theoretical spectrum as a function of the presence or absence of exchange interaction.

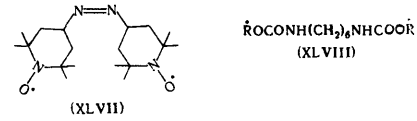
In contrast to the spectrum of the monoradical $\dot{R}$, the hyperfine structure of which consists of a triplet due to the ^{14}N nucleus (hyperfine structure constant $A_N = 15.6$ Oe) split by the β-protons ($A_H = 0.35$ Oe), in the spectra of the biradicals additional lines appear between the components of the triplet. Their number and intensity depend on the structure of the biradical. Thus the spectrum of the biradical (XXXIX), where the NO groups lie very close together, consists of five lines, which are regarded as due to the interaction of the two equivalent ^{14}N nuclei. In the spectrum of the biradical (XL), where there is an -OCO-OCO- group, additional lines do not appear and the spins behave independently. In the ESR spectrum of the biradicals (XLI) four additional lines appear, which Buchachenko et al. [48] believe to be due to the enhanced interaction between the unpaired electrons. The spectra of compounds (XLIII) and (XLIV) consist of triplets without additional lines, while in the spectrum of (XLV) there are again five lines, which are interpreted as indicating the occurrence of interaction between the two nitrogen atoms.

The monoradical (XLVIb) and the biradical (XLVI), which consists of large yellow crystals, were obtained by the oxidation of azine (XLVIa) [50]. The intensity of the ESR spectrum of the polycrystalline biradical is higher by a factor of 2.16 than the intensity of the polycrystalline monoradical containing the same number of molecules. In dimethylformamide the monoradical gives rise to the classical triplet with $A_N = 14.4$ Oe and $g = 2.0055$, while the biradical gives rise to a highly resolved triplet with $A_N = 7.2$ Oe. The authors explained these data by the occurrence of exchange interaction, the frequency of which is higher than that of the hyperfine interaction, i.e. $J \gg A$.



The width of the biradical line (2.4 Oe) does not differ much from the line width measured in the spectrum of the monoradical under the same conditions. (2.2 Oe). This means that the bond between the unpaired electrons is not strong enough to widen the ESR line due to dipole interaction.

The radical (XLVII) gives rise to a similar spectrum (Fig. 10a). [51] When the nitrogen atom in the iminoxy-groups is replaced by the ^{15}N isotope, three lines appear in the spectrum (Fig. 10b). This is accounted for by the interaction of the unpaired electron with the two nuclei of the ^{15}N atoms, which have a nuclear spin $I = \frac{1}{2}$ (case $J \gg A$, Fig. 1). The absence of splitting by the nitrogen atoms of the azine bridge shows that the electron exchange does not involve the system of σ-bonds. This is also indicated by the ESR spectrum of the biradical (XLVIII), in which there is no additional splitting by the ^{14}N nuclei of the heterochain bridge [48]:



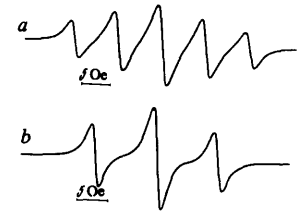


Figure 10. ESR spectra of the biradical (XLVII): *a*) unsubstituted biradical; *b*) biradical containing nitrogen-15.

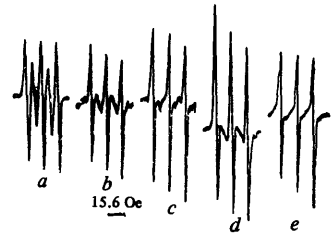
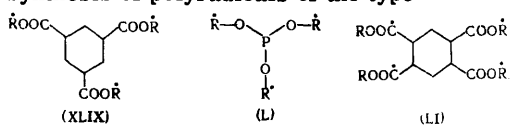


Figure 11. ESR spectra of the biradical (XLII) in different solvents: *a*) hexane; *b*) benzene; *c*) chloroform; *d*) carbon tetrachloride; *e*) acetic acid.

The ESR spectra of iminoxy-biradicals vary both with temperature and the nature of the solvent. Thus, when the temperature is raised, additional lines appear in the spectrum of compound (XL), the intensity of which increases with temperature. Fig. 11 presents the spectra of

the biradical (XLII)[47] in various solvents. Evidently here the shape of the spectrum is influenced not only by the viscosity of the solvent but also by the different solvation effects.

The synthesis of polyradicals of the type



(XLIX) (L) (LI)

on the basis of the monomeric biradical Ṙ has been described recently[52]. They have all been investigated by the ESR method.

It is interesting to note that the g-factors of iminoxy-biradicals are the same as those of the corresponding monoradicals and in none of the cases has it been possible to observe ESR signals with $g = 4$, which would correspond to $[\Delta m] = 2$ transitions.

Finally, the true mechanism of the exchange observed in the iminoxy-radicals has not yet been elucidated. Some workers[46-49] believe that the overlapping of the π-orbitals of the unpaired electrons and hence the exchange between the two halves of the biradical occur as a result of the bending of the molecules and the deformation of the chemical bonds and the angles between them, i.e. there is "conformational" exchange interaction when close mutual intramolecular approach of the paramagnetic fragments of the biradical takes place.

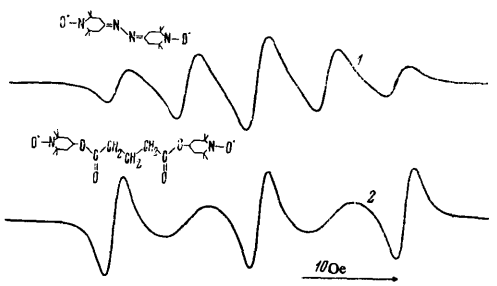
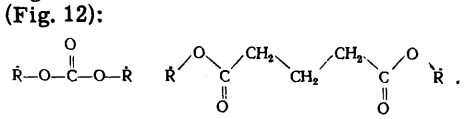


Figure 12. ESR spectra of the biradicals (XLVII) (curve *1*) and (LIII) (curve *2*).

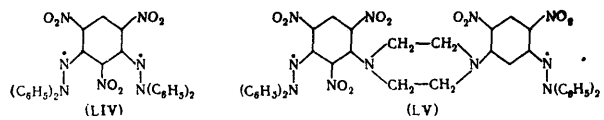
The influence of exchange interaction on line width has been investigated with the biradicals (LII) and (LIII) as examples[53] (Fig. 12):



(LII) (LIII)

When J varies in such a way that its average value $\overline{J}$ remains greater than A, the width of the central line and of the two outer lines remains constant, since their positions are independent of the changes in J. Other, intermediate lines become broader. This broadening is due to the modulation of the exchange integral J. When the exchange integral is expressed by formula (3), it is evident that its value depends on the extent of the overlapping $\Phi_A\Phi_B$ of the two wave functions $\Phi_A(1)$ and $\Phi_B(2)$, where $\Phi_A(1)$ is the orbital of the unpaired electron in one half of the molecule and $\Phi_B(2)$ is the orbital in the other half. When the extent of overlapping is low, the integral is large, and, correspondingly, a decrease in the extent of overlapping leads to a decrease of J. Since the biradical is not a rigid molecule, it can assume various configurations, each of which corresponds to a particular degree of overlapping $\Phi_A(1)\Phi_B(2)$ and different values of the integral J. This modulation of the integral J by intramolecular conformational changes does in fact constitute the relaxation mechanism which influences the biradical line width.

Biradicals of the hydrazine series (LIV) and (LV) have been synthesised recently and have been investigated by the ESR method[54,55]:



(LIV) (LV)

The theoretical spectrum of the biradical (LIV) is consistent with experiment (Fig. 13), provided that the unpaired electrons are localised in their halves and that each

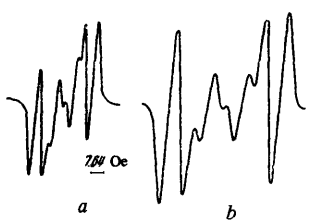
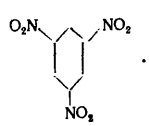
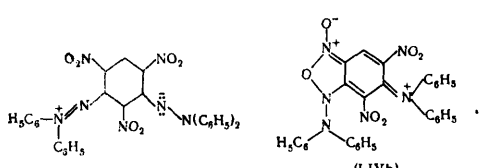


Figure 13. ESR spectra of the biradicals (LIVa) and (LIVb).

electron interacts only with the two non-equivalent nitrogen atoms and $A_{N_1}/A_{N_2} = 0.64$ and $A_{N_1} + A_{N_2} = 17.13$ Oe. This suggests that $J \ll A$ and there is thus no electron interaction via the bridge



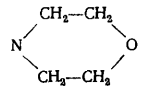
It is interesting to note that Heidberg and Weil[56] failed to observe the biradical form (LIV) in the oxidation of the bihydrazine monoradical and they attributed the singlet ground state of the resulting compound to the presence of ionic structures of the type



(LIVa) (LIVb)

The biradical (LV) gives rise to an ESR spectrum consisting of nine hyperfine structure components (Fig. 14). The theoretical spectrum containing nine components with intensity ratios 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 corresponds to four equivalent nitrogen atoms. Evidently each unpaired electron is not linked to its hydrazyl group and migrates from one half of the molecule to the other, i.e. in this case

$J \gg A$ and the electrons do interact with one another. Since in this case the interaction via the σ-bonds of the bridge



is excluded, it can be supposed that here the exchange mechanism is probably the same as in iminoxy-biradicals.

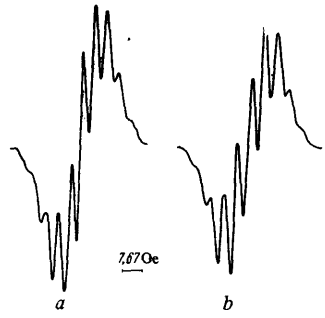
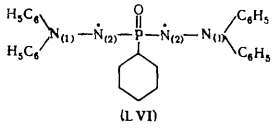


Figure 14. ESR spectra of the biradical (LV): *a*) experimental spectrum; *b*) theoretical spectrum.

A variation of the intensity of the spectrum of the biradical (LV) with temperature in the range between +60°C and −50°C could not be observed. Further reduction of temperature leads to a broadening of the ESR lines and the disappearance of the hyperfine structure. The spectrum of the supercooled solution shows one ESR line with a width of about 20 Oe between the points of inflexion and a g-factor of 2.0035. Other lines, characteristic of $S = 1$ as well as $|\Delta m| = 2$ transitions, were not observed. This may be due either to the low intensity of the $|\Delta m| = 2$ transition, which is weaker by 3 powers of 10 than the $|\Delta m| = 1$ transition, or to the breakdown of the intramolecular exchange bond between the two halves of the molecule on going to the supercooled state. In this case the anisotropic hyperfine structure is not resolved because of the dipole-induced broadening.

A biradical based on a phenylphosphonic dihydrazide has also been obtained[55]:

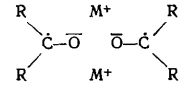


(LVI)

At the beginning of oxidation the ESR spectrum of the monoradical, consisting of seven hyperfine structure components, is observed. Comparison with the theoretical spectrum showed that the experimental spectrum results from the superposition of two quintets. The five lines in each quintet are due to the equally probable interactions of the unpaired electron with the two atoms of hydrazine. The isotropic hyperfine structure constant $A_N = 6$ Oe. The doublet with the constant $A_P = 10$ Oe must be assigned to the phosphorus nucleus. On further oxidation, the seven-component spectrum is converted into a quintet with the intensity ratios 1 : 2 : 3 : 2 : 1. The five lines of the hyperfine structure correspond to the delocalisation of each electron in its half of the molecule only, under conditions of interaction with the two nitrogen atoms of hydrazine. The form of the spectrum suggests that the nucleus of the phosphorus atom does not participate in splitting. There may be several reasons for the non-involvement of the phosphorus atom in hyperfine splitting and probably the main one is the breakdown of the p_π–d_π conjugation when the environment of the phosphorus changes on transition from the monoradical to the biradical. The constants A_{N_1} and A_{N_2} become larger by a factor of 1.5 than those of the monoradical, and the overall splitting $A_{N_1} + A_{N_2}$ increases from 12.2 to 17.6 Oe. An anisotropic hyperfine structure broadened by dipole interactions appears in the spectrum of the supercooled solution. No lines, additional to those with $g \simeq 2$, were observed.

VII. BIRADICALS OF METAL KETYLS

The study of the ESR spectra of the ketyls derived from hexamethyl- and pentamethyl-acetones showed that their hyperfine structure is due to splitting by protons in the ketone components, and furthermore that the unpaired electron is linked to the two equivalent nuclei of the alkali metal[59]. This finding can be accounted for on the basis of a dimeric structure of the ketyl molecule in which the two organic radicals are joined by two equivalent alkali metal ions:



The presence of dimers is also confirmed by optical spectra[57,59], which vary markedly with the concentration of the ketyls. Thus the spectrum of the fluorenonesodium ketyl in methyltetrahydrofuran at a high concentration shows a peak at 450 nm, while at lower concentrations this peak appears at 525 nm. Evidently there is a monomer–dimer equilibrium in the solution and since the spectra of the dimers and monomers are almost identical, it is evident that dimerisation does not involve any changes in the electronic structure. Thus the dimer molecules may be regarded as a kind of biradical system in which each electron spin belongs predominantly to one half of the dimer but is divided between the nuclei of the alkali metal. The ESR spectrum of solid ketyl solutions at 77°K shown in Fig. 15 is characteristic of triplet systems. The spectrum corresponding to the $|\Delta m| = 1$ transition results from the superposition of two spectra—a narrow central singlet and a broad doublet. With increase in the size of alkali metal ions, the doublet splitting increases from 118 Oe for the fluorenonelithium ketyl to 82 Oe for the fluorenonepotassium ketyl. The optical spectra at 77°K indicate the existence of both a monomeric and a dimeric form. The central singlet peak can be attributed to monomers (or dimers with a low degree of dipole interaction) and the doublet to dimers with a high degree of dipole interaction. Apart from the $|\Delta m| = 1$ transition, an absorption peak is observed when the field strength is reduced by one-half. This is due to the $|\Delta m| = 2$ transition (Fig. 15*f*). Its intensity is of the order of 10^{-3} of the intensity associated with the $|\Delta m| = 1$ transition.

The hyperfine structure of the spectra of liquid solutions of dimers with a high degree of dipole interaction is broadened by relaxation, while dimers with a low degree of dipole interaction give rise to a well resolved structure. Analysis of the Reitz–Weissman type of hyperfine splitting

in the spectra of ketyl dimers[11] shows that both the splitting by the ^{13}C nuclei and by protons in the ESR spectra of divalent- and trivalent-metal ketyls corresponds to the condition $A \gg J$. The rate of spin exchange between the two halves of the ion pair is thus much lower than the frequency of the hyperfine interaction and the spectrum of the dimer is similar to that of the monomer. The temperature variation of the absorption intensity is consistent with the low value of J.

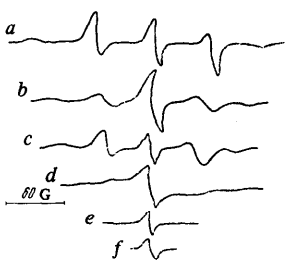


Figure 15. Spectra of paramagnetic ketyls in methyl tetrahydrofuran at 77°K; $|\Delta m| = 1$:
a) fluorenonelithium; *b*) fluorenonesodium; *c*) xanthonelithium; *d*) fluorenonebarium; *e*) fluorenonemagnesium; *f*) $|\Delta m| = 2$, fluorenonelithium.

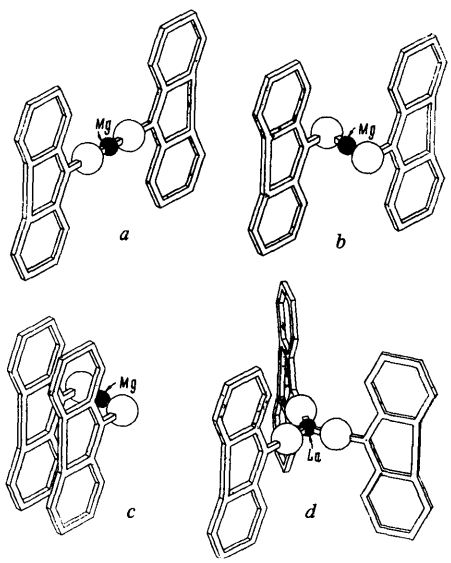


Figure 16. Possible structures of paramagnetic ketyls.

The possible structures of the dimeric ketyls can be inferred from the magnitude of the doublet splitting. Divalent-metal ketyls, apart from fluorenonebarium and fluorenonestrontium, give rise to spectra in which the half-width is about 10–15 Oe. Since divalent-metal ketyls do not dissociate, it can be assumed that the dipole interaction in them amounts to about 10 Oe. A possible structure of such a dimer is presented in Fig. 16*a*. The line half-width of 25 Oe observed in the spectra of trivalent-metal ketyls (Fig. 16*d*) indicates a high degree of dipole interaction. Structures of types *b* and *c* (Fig. 16) are possible in those cases where the line is broader and the dipole interaction more pronounced. In all probability there is an equilibrium between the dimeric forms and the most stable structure is determined by several factors: the structure of the initial ketone, the charge and the dimensions of the metal atom, and the nature of the solvent.

The data described above permit the following conclusions.

Electron spin resonance has proved most useful for the determination of the biradical nature of those compounds, the paramagnetism of which had not been demonstrated unambiguously by static magnetic susceptibility measurements and ortho–para conversion of hydrogen. For biradicals consisting of components separated by insulating groups, the ESR method permits certain inferences about their structure—the distribution of unpaired electrons. It follows from the hyperfine structure analysis of the spectra of biradicals of this type that each unpaired electron is localised in its own half and the biradical is a double monoradical.

However, there are as yet no convincing experimental data which would permit the analysis of the properties of systems of the type of Chichibabin's hydrocarbon in the triplet state (with "strong exchange interaction" between the two electrons). Possibly the absence of a hyperfine structure from the ESR spectra of certain biradicals of this type (and sometimes also the absence of an ESR signal at room temperature) is associated with the mechanism of the broadening, the main contribution to which comes from the spin–lattice relaxation. For this reason, the $|\Delta m| = 2$ transitions corresponding to the triplet state in these biradicals and also in the metal ketyl biradicals have been observed at very low temperatures only.

Atropisomers have not been investigated at all, although there is no doubt that the degree of coplanarity of the two halves of the biradical could be inferred from the hyperfine structure of the ESR spectra.

Further, more detailed study of the mechanism of the so called "conformational exchange" is essential.

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Processes Occurring in Solids Under the Action of Powerful Shock Waves

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The action of powerful shock waves on condensed materials can lead to a wide variety of physicochemical changes: polymorphic transformations, decomposition and synthetic processes, polymerisation of monomers, and defect-formation or conversely the formation of a more perfect structure. The study of these processes has shown that many of them take place exceptionally rapidly. The development of methods for the recovery of substances after the action of shock waves made it possible to employ high dynamic pressures for preparative purposes. Examination of the mechanism governing the compression of a substance by a shock wave shows that the transition from elastic monoaxial compression to bulk-phase compression may be identified with phase transformations as regards gas dynamics and thermodynamics and suggests that phase transitions in the shock wave cannot take place at pressures below the dynamic yield point of the substance. The presence of vigorous plastic flow in shock waves together with the operation of pressures reaching millions of atmospheres suggests that in many ways dynamic operations of this kind on various substances are comparable to methods combining high static pressures with shear stresses. Plastic flow in shock waves leads to the appearance of a characteristic mass-transfer mechanism which gives rise to diffusion processes during the very short period of shock-wave compression. Comparison of dynamic and static studies at high pressures reveals a very close correlation between them. However, a number of effects observed by shock-wave techniques are so far inconsistent with the phase diagrams of the corresponding substances.

CONTENTS

1. Introduction 392
2. Recovery of substances subjected to shock-wave compression 392
3. Ultrafast processes in shock waves 394
4. Ultrahigh pressures and shear deformation 395
5. The mechanism of shock-wave compression 395
6. Increase in the particle size of new phases in shock waves 396
7. Comparison of dynamic and static studies 398

I. INTRODUCTION

Numerous experimental data show that, under the action of shock waves due to the detonation of explosives and impact of bodies moving at a high velocity, various chemical and physicochemical transformations take place in condensed substances. In particular, certain substances subjected to the action of shock waves undergo polymorphic transformations. Attention was drawn to this for the first time by Bancroft et al.[1], who investigated the shock compressibility of iron and observed at 130 000 atm a break in the Hugoniot curve†, which they accounted for by polymorphic transformations occurring in iron under these conditions. Subsequently such breaks were observed also in the Hugoniot curves for a number of other substances, for example carbon[2], quartz[3,4], marble[5], potassium bromide and chloride[6-8], and other compounds[9]. Apart from polymorphic transformations, phenomena such as fusion[10,11] and plastic flow on transition from monoaxial elastic compression to bulk compression can also be reflected in breaks in the Hugoniot curves[3,4,12].

An important distinctive feature of these transformations in shock waves is their unusually high rate. Whereas the formation of new phases in static experiments requires times reckoned in seconds, minutes, and sometimes hours and even longer periods, in shock waves these processes are completed in fractions of a microsecond.

The observation of breaks in Hugoniot curves is only a part of the investigation of the transformations in substances under the action of shock waves. Successful studies of this kind permit the determination of the parameters of the shock-wave compression during which the transformation took place, which is itself of scientific interest. On the other hand, in order to determine what transformation is undergone by the substance and whether it is reversible or irreversible under the given conditions, it is desirable to recover the test specimen in the state which obtains at the instant when the shock wave ceases to operate. Such methods have been developed.

† The Russians refer to this as the shock compressibility curve or the adiabatic shock curve (Ed. of Translation).

2. RECOVERY OF SUBSTANCES SUBJECTED TO SHOCK-WAVE COMPRESSION

The first data derived from studies of substances recovered after shock-wave compression were published by Ryabinin[13] in 1956. Novosibirsk investigators[14] began their study by a similar method and later applied other procedures also[15]. Designs of cylindrical and flat iron and copper tubes, whereby substances can be recovered after being subjected to the action of detonation of charges consisting of the most powerful standard explosives, were developed in the laboratory of one of the authors[16,17]. The pressure which then arises in the tube depends not only on the power of the explosive charge used and the duration of its operation but also on the initial density and compressibility of the test substance. With dense comparatively compressible substances the pressures reached more than five million atmospheres and yet the test specimens were satisfactorily recovered. Readily compressible substances of low density are recovered with greater difficulty.

Similar studies are being carried out also outside the Soviet Union. For example the Japanese investigator Kimura[18] developed an unusual recovery method, while Israeli scientists[19] use a method similar to that of Ryabinin.

American investigators have also reported studies on the recovery of specimens (see, for example, Wackerle[3] and DeCarli and Jamieson[20]) but little information is available about the recovery methods which they used.

The study of specimens recovered after shock-wave compression confirmed that the breaks in the Hugoniot curves can indeed be caused by phase transformations. For example, the suggestion by Alder and Christian[2] that the break in the Hugoniot curve for graphite corresponds to the transformation of the latter into diamond was confirmed by DeCarli and Jamieson[20], who succeeded in obtaining diamond from graphite, containing regions of rhombohedral structure, after shock-wave compression at a pressure of up to 300 000 atm during 1 ms. The present authors also achieved partial conversion of ordinary graphite into diamond with a yield of 3%.

It has been shown[21] that there is also a break in the Hugoniot curve for hexagonal graphite-like boron nitride. Studies on the recovery of specimens confirmed that the break is due to the polymorphic transformation of boron nitride into a denser modification, namely the hexagonal wurtzite-like modification of borazon. Later it was shown that, together with the hexagonal wurtzite-like borazon, there forms also a certain amount of a cubic sphalerite-like modification of this ultrahard substance.

Batsanov and coworkers[22], who studied the shock-wave compression amorphous boron nitride synthesised in their laboratory, obtained a new form of this compound. Kennedy and Benedick[23] showed that wurtzite-like cadmium sulphide is converted in the shock wave into a modification with a structure of the sodium chloride type during a period not greater than 1 μs. Batsanov and Deribas[14] reported the transformation on shock-wave compression of the usual form of neodymium oxide into a new phase.

Deribas and coworkers[24] studied the effect of shock-wave compression on silica and obtained a number of interesting results. Wackerle[3] also recovered specimens of single-crystal silica subjected to shock-wave compression. Traces of coesite were detected by Deribas et al.[24] and by ourselves in silica subjected to shock-wave compression. Wackerle[3], Deribas et al.[24], and earlier DeCarli and Jamieson[25] showed that, when silica is compressed by sufficiently powerful shock waves, it is converted into a vitreous form although the maximum temperature of the specimens at the instant of shock was much less than the melting point of this compound. Albite underwent a similar transformation in the experiments of DeCarli and Jamieson[25]. Secrist and Mackenzie[26] attribute considerable importance to this method of preparation of substances in the vitreous state.

Shock-wave compression may lead not only to polymorphic transformations but also to chemical changes. For example, Kimura[18] showed that shock-wave compression of a mixture of iron and zinc oxides leads to the formation of ferrites. We achieved certain syntheses as a result of shock-wave compression. For example, a mixture of sodium and magnesium fluorides was almost completely converted into sodium fluoromagnate $NaMgF_3$, and a mixture of metallic indium and phosphorus gave rise to a satisfactory yield of indium phosphide. The shock-wave compression of a mixture of elemental boron and lithium nitride and also of boron oxide and ammonium chloride gave rise to the formation of small amounts of boron nitride, the reaction products containing its dense modifications—cubic and hexagonal borazon.

Ryabinin[13] noted significant defect formation in sodium chloride subjected to shock-wave compression, the decomposition of lead nitrate to the dioxide, the decomposition of magnesium carbonate to a mixture of magnesium oxide and carbon dioxide, and pyrolysis of hydrocarbons.

A large number of chemical reactions were observed by Batsanov and Deribas and coworkers. They noted the decomposition of a number of carbonates[27], sulphates, and nitrates[28]. By analysing their results, these investigators found that the changes occurring in the test substances subjected to shock-wave compression are associated in the first place with their thermodynamic stability. Under constant shock-wave compression conditions, the substances decompose if the heat of their formation is below a limiting value, the extent of decomposition being greater the lower is the heat of formation. If the heat of formation of the compound exceeds the limit, the effect is restricted to the formation of chemical or structural defects. In the most stable compounds, a more perfect structure of the crystal lattice is formed. The same investigators noted a number of interesting phenomena in the study of the effect of shock waves on potassium nitrate.

Our own data[16,29] confirmed the results of Batsanov et al.[28] Substances with high chemical and thermal stability, such as alkaline-earth fluorides, alumina, etc. acquire a more ideal crystal structure on shock-wave compression, approaching in their properties well-formed single crystals. However, since we used more powerful explosive charges, we observed the decomposition even of those substances which remained completely unchanged in the earlier experiments[13,27,28]. For example, copper sulphate was partially decomposed to cupric oxide and partially to metallic copper. Compounds such as PNO, Li_3N, $NiF_2 . 2H_2O$ etc. were found to decompose. Partial or complete decomposition of a number of metal oxides was observed (oxides of antimony, nickel, iron, titanium, molybdenum, tungsten, etc.), the free metal formed in the decomposition being sometimes observed in the form of large beads (1–3 mm) in the tubes used to recover the substance.

It has been established that porous substances can be significantly contaminated by the material of the tube wall, and therefore many chemical reactions may be due to the usual high-temperature interaction with the iron in the tube[16,30].

It is interesting that many dispersed substances (for example magnesium, nickel, and calcium fluorides) are converted into materials with much larger crystals after shock-wave compression[16]. Before shock-wave compression magnesium and nickel fluorides consisted of powders of very small particles, which gave rise to distinct powder diffraction patterns even without rotation of the specimens and proved to be optically isotropic on examination in a polarisation microscope. After shock-wave compression the particles of these substances became significantly larger, so that powder diffraction patterns recorded without rotation showed distinct reflections from individual crystals and the anisotropy characteristic of the substances became apparent in polarised light.

Many organic substances were found to polymerise under the action of shock waves[31]. Studies of the shock compressibility of monomeric and polymeric acrylamide showed that the polymerisation process takes place at an enormous rate when the density of the monomer reaches that of the polymer under shock conditions[32]. It was shown that the energy evolved in polymerisation intensifies the shock wave. (The dimerisation of cyclopentadiene under the influence of the detonation of tetryl was achieved by Vereshchagin and coworkers as early as 1945.[35]) Barkalov et al.[33] suggested the possibility of the shock polymerisation of infinitely large monomer blocks (polymerisation detonation).

3. ULTRAFAST PROCESSES IN SHOCK WAVES

The above findings show that, when various substances are acted upon by shock waves, the resulting processes do indeed take place at high rates. This applies also to non-diffusion reactions (certain polymorphic transformations) and reactions for which the occurrence of diffusional processes is inevitable (for example, syntheses and decompositions)‡.

At the present time there are no generally accepted hypotheses which would account for the unusually high rates of physicochemical reactions in shock waves. Probably this is caused in the first place by the lack of the necessary experimental data, for example, such as those on the dependence of the degree of conversion and the particle size of the new phase, on the parameters of shock-wave compression (pressure, temperature, time of operation of high pressure) and the initial state of the substance (in particular its degree of dispersion).

Roughly speaking all physicochemical changes occurring under the action of a shock wave (polymorphic transformations, conversion into the vitreous state, formation of a more perfect crystal lattice in relatively weak shock waves and defect formation in powerful shock waves, decompositions, syntheses, and polymerisation) can be divided into two classes. The first class includes those transformations which occur during the period of operation of the high pressure during shock-wave compression. Polymorphic transformations and polymerisation phenomena undoubtedly belong to this class. Indeed, as already stated above, shock-wave compression curves for substances undergoing polymorphic transformation or polymerising under the action of shock waves show breaks demonstrating that the corresponding phenomenon takes place directly in the shock-wave front. The first class also includes synthetic reactions with formation of phases which are thermodynamically stable only at a high pressure. For all other transformations, which belong to the second class, there is unfortunately no proof at present that they occur during the operation of the shock waves and not, say, during a much longer period under the action of high residual temperatures.

The effect of the high pressures generated in the shock wave cannot alone account for the enormous increase in the rate of processes. A series of investigations showed, in agreement with theory [36-40], that, on increasing the pressure, diffusional processes are not only not accelerated but in fact retarded as a rule. A wide variety of explanations have been put forward for this phenomenon. For example, Hilliard and Cahn [41] attribute the decrease of the rate of diffusion at high pressure merely to a decrease of the equilibrium concentrations of vacancies and not a decrease in their mobility. (So far there are no data about diffusion along grain boundaries.) In the same publication the authors write that at high pressures the rate of transformations should decrease mainly due to the decrease of atomic mobility. On the other hand, Pozin et al. [42] believe that the rate of "true" solid-phase reactions should increase on raising the pressure due to the increase of contact between the grains. Then, of course, it may again fall due to the decrease of the diffusion coefficient.

The ultrahigh rates of processes in shock waves have been attracting the attention of an increasing number of scientists, although ten years ago it was generally believed that during shock-wave compression of heterogeneous polycrystalline mixtures "such a wide variety of complex phenomena may be encountered that there are no means for a complete explanation" [43].

Attempts are now being made to investigate non-diffusional processes. Thus, after a long discussion, Anders and Lipschutz [44,45] concluded that diamonds in meteorites are formed by a direct solid-phase transformation under the action of the shock wave produced on impact of the meteorite against the earth. They believe that the usual mechanisms governing the appearance of a new phase (generation and growth of nuclei) cannot operate in shock waves because the process is extremely short-lived. Wentorf and Bovenkerk [46] share this view and note that the growth of nuclei from the melt also cannot play a significant role because the time is too short and the probability of any appreciable extent of diffusional processes during this period is low. Libby [47] likewise supports this view and suggests that polymorphic transformations in a shock wave take place directly over the entire bulk of the substance without the usual requirement of the growth of a new phase from the previously formed crystallisation centre. Another aspect of Libby's views is that the formation of new phases in a shock wave consists of two stages: the formation of "an activated complex" (the substance compressed to the metallic state is usually understood as the activated complex§) and the conversion of this complex, on expansion, into a new phase, which is thermodynamically stable at the temperatures and pressures corresponding to the loss of stability by the activated complex (i.e. the metallic state of substance). It is believed that shock-wave compression of two different modifications of the substance (for example, graphite and diamond) leads to the formation of identical activated complexes.

In an examination of decomposition of synthetic processes in shock waves one must inevitably invoke one or other diffusion mechanism, whereby one can explain how metal and oxygen atoms, for example, which are adjacent in the crystal lattice of the initial oxide, are sorted out after shock-wave compression and separated in space.

At the same time it appears unlikely that the usual diffusion mechanism, involving the motion of individual atoms or ions (or whole groups of atoms) among the surrounding neighbouring species, which are strongly compressed at the high pressures existing behind the shock-wave front, can lead to the formation, in a period of the order of 10^{-5}–10^{-7} s, of the particles of a new phase, which in practice reach dimensions of 0.1 mm and more. This is contradicted by abundant experimental data showing a decrease of the rate of diffusion with increasing pressure (see, for example, Refs. 36–40).

Probably the key to the solution of the problem of the unusually high rates of reactions of the first class should be sought in experiments on the effect of ultrahigh static pressures in combination with shear of the compressed

‡ In the light of the above findings the view expressed by Dachille and Roy [35] sounds a little odd: ".....it is clear that, in experiments with shock-wave pressures which act upon the specimen during periods of the order of a microsecond, it is difficult to achieve considerable chemical or structural changes in the specimen". In contrast, one may note that Kormer et al. [8] showed by direct experiments that in the compression of potassium chloride and bromide by a powerful shock waves phase transitions (fusion) take place over a period of 10^{-11} s.

§ In agreement with theory, numerous experiments show that sufficiently high pressures convert all substances into a metallic state (see, for example, Refs. 48–51).

specimen. Here the idea of the possibility of such an analogy for polymorphic transformations was put forward by Douglas et al.[52]

4. ULTRAHIGH PRESSURES AND SHEAR DEFORMATION

Many investigators have shown that at usual pressures shear deformation can have a significant effect on the rates of chemical and phase transformations in solids (see, for example, Refs. 53 and 54). Similar phenomena might have been expected also at ultrahigh pressures. However, it was found that under these conditions shear deformation not only accelerates the processes but also leads to a radical change in their character. For example, Bridgman[55-58] established that bismuth oxide Bi_2O_3 subjected to the simultaneous action of a pressure of the order of 25 000–50 000 atm and shear deformation breaks down into metallic bismuth and free oxygen. Under these conditions tin dioxide lost part of its oxygen and was converted into the monoxide, and metallic copper and elemental sulphur interacted with formation of copper monosulphide.

Vereshchagin and coworkers devoted much attention to this technique[59-66]. They showed that pressure combined with shear accelerates certain polymorphic transformations, lowers the temperature of some phase transitions, sometimes gives rise to phase transitions which are not observed in the absence of shear (for example, in metallic lithium), leads to the decomposition of a number of compounds (copper sulphide, lead oxide, molybdenum trioxide, and others), and permits a number of syntheses from the elements (iron, nickel, and cobalt sulphides and magnesium and zinc phosphides).

A general feature of these processes is that high pressures make their occurrence thermodynamically possible but their rates are fairly slow due to diffusion-dependent limitations. On the other hand, when a shear stress is applied to the test specimen during the operation of these pressures¶, the rates become much higher and frequently the process goes to completion during the period of the shear stress. For example, in a study of the effect of high pressures on potassium hexacyanoferrate(III), Larsen and Drickamer[67] showed that shear stresses accelerate the decomposition of this compound into potassium hexacyanoferrate(II), cyanogen, and free iron by a factor of 10^{14}. Enikolopov et al.[68] observed that at static pressures of tens of thousands of atmospheres many monomers virtually do not polymerise without the artificial creation of polymerisation centres. On the other hand, at the same pressures combined with shear polymerisation takes place at high rates without the introduction of any additional active centres.

Teller[69] believes that shear phenomena at high pressures can play a decisive role in chemical processes, in particular in the conversion of an exothermic reaction into an explosive process. However, he reduces the entire role of shear deformation to the accumulation of energy in the substance, which in turn helps overcome the activation barrier between the initial and final states. Leiserowitz et al.[19] draw a complete analogy between experiments on shock-wave compression and experiments on the effect of pressure combined with shear without taking into account the specific features of the effect of the shock-wave front.

¶ It is useful to note here that the plasticity of most substances increases with pressure[53,54].

5. THE MECHANISM OF SHOCK-WAVE COMPRESSION

Let us consider the mechanism of the compression of a substance by a shock wave. When the substance does not undergo any transformations on shock-wave compression, the shock-wave compression curve does not show any unusual features. The width of the shock-wave front (the region between the initial and final states of the substance subjected to shock-wave compression) is then very small: of the order of the free path in gases[70] and probably of the order of the interatomic distances in solids. On the other hand, if the substance does undergo a transformation on shock-wave compression, experiments show that the shock compressibility curve shows a break in one or other direction depending on the nature of the transformation, when the intensity of the shock wave is just below the intensity corresponding to the transformation. As predicted by Zel'dovich[71] and subsequently frequently confirmed experimentally, the shock-wave front then becomes diffuse and broadens, since the transformation requires a finite time.

If the transformation under shock-wave conditions takes place with increase in volume, the shock compressibility curve becomes steeper. The pressure profile in the stationary shock-wave front in such a substance is of the form shown in Fig. 1*b*. In principle, waves with such a profile are capable of steady-state propagation without the supply of energy from outside. A convincing example of the existence of such waves is the detonation waves in explosives.

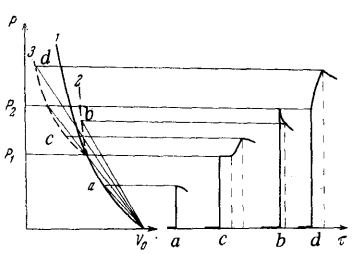

Figure 1. Hugoniot curves for various substances and the corresponding shock-wave profiles:
1) without transformations; *2*) transformation with increase in volume; *3*) transformation with decrease in volume;
a) pressure profile in the shock wave in the absence of transformations; *b*) transformation with increase in volume; *c*) transformation with decrease in volume; *d*) transformation with decrease in volume at sufficiently high pressures.

A break in the direction of smaller volumes has been observed for the polymorphic transformations investigated hitherto. Then, as shown by experiment, the shock wave loses stability over certain range of pressures. Initially a shock wave with an amplitude corresponding to the pressure of the onset of the phase transformation is propagated through the substance and then a slower second wave, in which the transformation itself occurs. The width of the front of the second wave corresponds to the duration of the transformation (Fig. 1*c*). At a pressure higher than P_2 (Fig. 1*d*) a single shock wave with the pressure profile shown in Fig. 1 is propagated in the substance undergoing polymorphic transformation; the width of the shock-wave front corresponds to the duration of the transformation.

Thus the complex form of the shock compressibility curve and the increase in the width of the shock-wave front constitute a direct demonstration of the occurrence of the transformation in the wave front, i.e. during a period less than 10^{-6} s.

Probably the unusually high rates of transformations with which we deal in these cases are due to the specific features of the compression of the substance by the shock wave. Shock-wave compression is a non-isentropic process. On the other hand, the flow before and beyond the shock-wave front in the rarefaction wave (in the system of coordinates associated with the front) is an isentropic process. Consequently the increase of entropy occurs in the front itself over a region corresponding to its actual width[70]. Physically the growth of entropy implies a transition from ordered translational motion of atoms or molecules of the substance in front of the wave into random motion in the front itself. This takes place in consequence of the non-head-on collisions between the moving atoms and the atoms already present in the front (in the system of coordinates associated with the shock-wave front). Thus in the shock-wave front there is always a sharp deviation from translational motion, i.e. components of atomic motion along the wave front appear.

From the macroscopic point of view, the shock wave effects monoaxial compression of the substance. When solids are compressed by shock waves with amplitudes less than the dynamic yield point, transverse displacements due to non-head-on collisions of atoms should also arise in the wave front. However, the energy of such displacements is less than the bonding energy in the crystal lattice. Therefore ultimately the atom remains at its original site but in an excited state. In this case compression leads to a change only in the interatomic distances along the wave, but the distances along the wave front remain the same. Such deformation of the crystal lattice is thermodynamically unfavourable, since a potential energy of displacement appears in addition to the potential energy of compression, so that the total potential energy is not a minimum[71].

Minimum potential energy is attained on compression from all sides when the crystal lattice undergoes a symmetrical deformation. Symmetrical compression of the crystal lattice by the shock wave occurs at compression pressures in excess of the dynamic yield point. Then tangential stresses in the solid exceed the critical value and the material begins to flow. In an examination of the process at an atomic level this implies that in a non-head-on collision the displacement of atoms along the shock-wave front becomes so great that the atoms acquire a certain freedom and no longer return to the previous site but remain in the coordination environment corresponding to the thermodynamic conditions (P, T) created on compression. If according to the phase diagram the substance should not undergo polymorphic transformations on shock-wave compression above the dynamic yield point, the state of the substance behind the shock-wave front corresponds to the initial crystal lattice but with lower parameters due to compression from all sides. On the other hand, if a new lattice is thermodynamically more favourable under the given conditions, a polymorphic transformation takes place.

Since a displacement of atoms from the equilibrium position, due to the passage of the shock wave, takes place in the matrix of the initial crystal lattice, it is possible that Libby's hypothesis[47], that the state of a substance subjected to shock-wave compression does not depend on the choice of the initial modification, is not always valid. This can be demonstrated by the fact that the Hugoniot curves for pyrolytic graphite and graphite containing domains of a rhombohedral structure are different. In the first case a transition to the diamond structure is not observed[72].

Two conclusions follow from the above discussion. Firstly the transition from elastic monoaxial compression to bulk-phase plastic compression is equivalent, as regards thermodynamics and gas dynamics, to a polymorphic transformation. Secondly the phenomenon of polymorphism under the action of a shock wave cannot occur at pressures below the dynamic yield point of the initial substance.

A change in volume along the shock compressibility curve during a polymorphic transformation is evidence that the transformation takes place to a very marked extent. In principle, one cannot exclude in this case the possibility that the rearrangement of the initial crystal lattice directly in the shock-wave front leads to the formation of large single crystals of a new phase, which then break down in the expansion wave after the removal of the pressure. However, it is probably more likely, and this follows from the considerations adduced above, that a large number of very small nuclei of a new phase, randomly distributed in relation to one another, are formed in the shock-wave front. Indeed it is difficult to suppose that the chaotic conditions arising in the shock-wave front simultaneously over the entire surface of the latter lead to a rigorously ordered arrangement of atoms corresponding to the crystal lattice of the new phase, i.e. it is essentially difficult to postulate an epitaxial growth of the crystals of the new phase in the shock-wave front. However, it is then necessary to explain how the substance consisting throughout of nuclei is converted into relatively large crystalline formations observed in the recovery tubes. Certain considerations concerning this problem will be put forward below in an examination of the possible mechanism of chemical reactions in a shock wave.

6. INCREASE IN THE PARTICLE SIZE OF NEW PHASES IN SHOCK WAVES

In crystalline lattices the position of atoms and the interatomic distances are determined by the equilibrium between forces of attraction and repulsion. The depth of the potential well in which each atom is located characterises the strength of the chemical bond. With increase of pressure, the atoms of the crystal lattice approach one another, the role of repulsion forces becomes more important, and the strength of chemical bonds falls. According to Kapustinskii[48], "the universal metallic state of matter", characterised by a complete disappearance of chemical differences between atoms and hence by the disappearance of all chemical bonds, arises when a substance is subjected to a sufficiently high pressure (about 10^8 atm).

In shock-wave compression we usually deal with much lower pressures (10^5–10^6 atm) and therefore there can be only a weakening of chemical bonds. The situation is of course complicated by the fact that the temperature of certain substances subjected to shock-wave compression can reach tens of thousands of degrees when the intensity of shock waves is high. It is reasonable to suppose that the weakening of the strength of chemical bonds will be different in different cases. Let us consider a compound AB which decomposes on increase of pressure. One can imagine a case such that, under normal conditions (P_0, T_0), A–B bonds are energetically more favourable ($2E_{A-B}$ is greater than $E_{A-A} + E_{B-B}$), while at sufficiently high P and T the bonds A–A and B–B become energetically more favourable, i.e. at P_0 and T_0 the phase AB is stable, while

at P and T the stable phases are A and B. In this case, after attainment of the pressure P and the temperature T, the thermodynamic conditions for the stability of the AB phase break down and decomposition of the compound becomes possible.

Examples of such reactions, found in the study of the effects of high static pressures on various substances, have been described in the literature. For example, according to Popova et al.[73], cuprous oxide disproportionates into metallic copper and cupric oxide at a pressure of 180 000 atm and 2000°C. According to Hoffman[74], Pb_2O decomposes at 2000 atm with liberation of metallic lead, while PbO_2 decomposes at 12 000 atm into lead oxide (PbO) and oxygen. Arkharov and Bulychev[75] have stated that an increase of pressure favours the decomposition of the $Fe_{1-x}O$ phase into iron and Fe_3O_4 with a simultaneous decrease of the number of defects in the initial phase. DeVries[76] showed that at 25 000 atm and 1500°C Al_2SiO_5 decomposes into corundum and a silicate melt. On the other hand, it has been stated[35] that Coesu succeeded in obtaining at a pressure of 40 000 atm a substance with the composition $Al_2O_3 \cdot 3SiO_2$, which cannot be synthesised at the normal pressure. All these processes take place relatively slowly. Thus high pressures and temperatures in the shock wave create a thermodynamic background which determines the *possibility* or *impossibility* of the occurrence of both polymorphic transformations and chemical reactions.

The momentum imparted to atoms by the shock wave is insufficient for virtually instantaneous interpenetration of the reacting species of the initial reaction mixture. It is sufficient to recall that α-particles moving at velocities higher by 3–4 powers of 10 than the velocity of matter in shock waves are stopped by layers a few tens of atoms thick. It would appear that even less comprehensible is the occurrence of decomposition processes in which separation of different types of atom from one another and not mixing at a molecular level is required, or the occurrence of synthetic processes where both requirements must be met. However, we believe that the occurrence of plastic flow makes it possible to overcome this difficulty. Here we have in mind the occurrence of extensive plastic flow of the substance in the recovery tubes. This is indicated by the significant residual deformation of the tubes themselves.

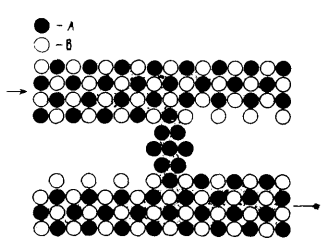

Figure 2. Scheme describing the decomposition of a compound AB during plastic flow in the rarefaction wave.

Fig. 2 presents a highly qualitative scheme representing chemical processes in the presence of plastic flow. When two layers of the substance are displaced relative to one another, the nuclei of phase A, located between them, can be regarded as a kind of roller about which oscillations are executed. With some approximation, phase A under these conditions can be regarded as a solid and phase AB as a liquid, since the strength of A–A bonds under these conditions is greater than that of A–B bonds. When the two layers of phase AB are displaced relative to one another, they transport past the nucleus, in its immediate vicinity, a multiplicity of atoms of both kinds. Since the time required for the rearrangement of electron shells (10^{-13}–10^{-14} s) is much shorter than the time required for contact between atoms (it is easy to calculate that for a plastic displacement over a distance of the order of 1 mm†, dimensions of a single atom of 2 Å, and duration if shock-wave compression of 10^{-5} s, the time required for contact between two atoms is 2×10^{-12} s) it follows that all the atoms A passing in the immediate vicinity of the nucleus have sufficient time to combine with the latter and this in fact may be the mechanism of the growth of the nuclei of the new phase. Of course, the same mechanism can operate also in the growth of phase B.

Thus, in contrast to the usual diffusional growth of crystallisation centres, in which each atom must find its way to the new phase, pushing apart its neighbours by virtue of the energy of thermal motion, in the growth of new-phase nuclei behind the shock-wave front the entire mass of the initial phase is transported by the plastic flow in the vicinity of the crystallisation centres and the required atoms combine selectively with the particles of the new phase undergoing continuous growth during this process.

An attempt may be made to estimate the dimensions of the new-phase particles, which can form by the mechanism proposed. For simplicity, it will be assumed that (a) the new phase forms in the plastic flow of an ideal crystal lattice of the initial phase, (b) the initial "nucleus" is a single atom X, (c) only atoms from a monatomic layer of the initial phase passing during the plastic flow above (below) the crystallisation centre can add to the latter, and (d) different crystallisation centres do not stick together.

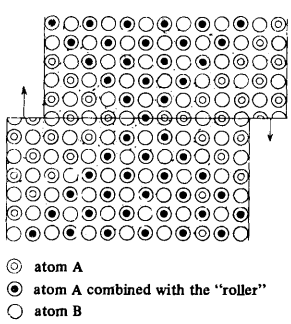

Figure 3. Representation of the phase AB in plan form along the slip plane during plastic flow; the atoms A which add to the initial atomic nucleus during plastic flow in the shock wave are indicated.

Fig. 3 shows in plan form the phase AB along the slip plane in plastic flow. The A atoms indicated add to the initial atomic nucleus when the AB phase moves in the vicinity of the roller being produced. The calculation of the number of atoms which can be combined into a new phase is simple. When two layers are displaced relative to one another over a distance H, the structure of each

† In practice up to 3–5 cm.[16]

layer is as shown in Fig. 3, and the distance A–B is L, then N, the number of atoms captured by the roller during the displacement of the layers, is defined by the expression,

$$N = 1 + 2\left[2 + 3 + \ldots + \left(\frac{H}{2L} - 1\right) + \frac{H}{2L}\right] = 1 + \frac{H}{2L}\left(\frac{H}{2L} + 1\right) \simeq \frac{H^2}{4L^2}.$$

For example, for $H = 1$ mm and $L = 1$ Å, we have

$$N = \frac{1}{(2 \times 10^{-7})^2} = 2.5 \times 10^{13} \text{ atoms.}$$

When the particles of the new phase are assumed to be cubic, their dimensions are $\sqrt[3]{2.5 \times 10^{13}} = 2.92 \times 10^4$ atoms $\simeq$ $2.92 \times 10^4 \times 1 \times 10^{-7} \simeq 0.003$ mm.

The same mechanism of the growth of new-phase particles can also operate in polymorphic transformations in the shock wave. In this case the relative motion and rotation of the nuclei insures their adhesion in a definite regular crystallographic arrangement. The return to the initial state on removal of pressure in those cases where polymorphism does not obtain is ensured by the usual processes, which also occur on removal of pressure in static experiments.

It is readily seen that in shock-wave compression of finely crystalline substances the random states of the single-phase particles in contact are identical and the particles are combined into a single mass during the plastic flow of which there is a possibility of the growth of larger particles. This can account for the increase in size and the improvement of the structure of a number of substances after shock-wave compression. Probably the maximum size of crystalline particles in the recovered specimen is restricted by the dynamic strength of the substance and the pressure gradient in the rarefaction wave. An approximate estimate of this size for real dimensions of explosive charges shows that it can reach several millimeters. However, it should be noted that plastic flow which, on the one hand, favours the growth of very small crystalline phase nuclei, can, on the other hand, break down fairly large particles.

The following considerations can be put forward concerning the polymerisation phenomenon in shock waves. Calculation of the temperature of acrylamide immediately behind the shock-wave front shows that, over the entire pressure range, between 20 000 and 80 000 atm, it is less than the melting point of the compound. This means that the polymerisation takes place in the solid phase. It may be suggested that the rearrangement of the crystal lattice, which leads to a decrease of the number of defects, plays an important role also in polymerisation process. At the very beginning of the crystal lattice rearrangement zone, active centres initiating polymerisation may arise. The polymerisation itself probably takes place during the formation of the new crystal lattice. The unusually high, explosive rates of polymerisation are probably due to the favourable relative orientation of the molecules in the monomer crystal[77], particularly when it is remembered that the monomer is compressed to the density of the polymer. The "roller" mechanism of the growth of polymer chains is of course also possible.

7. COMPARISON OF DYNAMIC AND STATIC STUDIES

The most interesting aspect of the investigation of the action of shock waves on matter is comparison of static and dynamic studies. However, methodologically it is a fairly difficult task. The point is that in static studies the aim is as a rule to investigate the P–T diagrams, while in dynamic studies data on P–V diagrams are most readily obtained. Experimental determination of temperatures in shock waves has been achieved for an extremely limited range of compounds[6]. In other cases one is restricted to calculated data and furthermore only the Hugoniot curves without breaks or, more precisely, only those sections of Hugoniot curves which correspond to pressures below the first break, are susceptible to exact calculations. At the present time such calculations have been made mainly for metals[3].

Another methodological difficulty encountered in the comparison of static and dynamic data consists in the fact that in most cases static experiments are performed at pressures up to 100 000 atm, while published dynamic data usually refer to pressures starting with 50–100 000 atm. A decrease of the initial density (increase of porosity) of the test specimen increases the temperature in the shock wave, which permits the use of dynamic methods in the region of the P–T diagram above the Hugoniot curve. The same result can be obtained when preheated monolithic specimens are investigated. The region of the P–T diagram below the Hugoniot curve of the monolithic specimen can be penetrated to some extent by carrying out preliminary cooling of the specimen or be applying special methods of shock-wave compression in which the final pressure in the specimen is attained in stages. This lowers the temperature developed in the specimen at the same final pressure. However, the region of the P–T diagram immediately adjacent to the pressure coordinate is in principle inaccessible to dynamic investigations.

At the present time comparable experimental data derived from dynamic and static studies are available for only a small range of substances. These are mainly metals. For example, it is possible to compare the P–T diagrams for iron[78] with data obtained in dynamic studies[79,80].

McQueen and Marsh[79] present data for the Hugoniot curve of the iron calculated from the results of an investigation of the shock compressibility of iron. The point of intersection of the P–T Hugoniot curve with the curve for the α-Fe $\rightleftharpoons$ ϵ-Fe phase equilibrium agrees fairly well, as regards pressure, with the beginning of the break in the shock compressibility curve (131 000 atm). Jonson et al.[80] studied the temperature variation of the phase-transition pressure in iron by subjecting to the action of shock waves specimens which had been first heated or cooled. It was assumed that in the shock-wave compression the temperature virtually did not change and the transition pressure was estimated from the depth of the iron layer in which irreversible phase transitions were observed and from the rate of decay of the waves in iron, which the author determined. Despite these assumptions and other simplifications made in the interpretation of the results, the data obtained agree entirely with the phase diagram for iron. It is surprising that, at the time of the publication of their paper, Jonson et al. were apparently unaware of the existence of the ϵ-modification of iron. The existence of this modification, which is stable at high pressures, was confirmed by Jamieson and Lowson[81] one month later in static experiments, but this result might have been suggested also by the work of Balchan and Drickamer[82].

It is also interesting to compare the data from static and dynamic studies on germanium. Two breaks were found in the Hugoniot curve for this element[83], corresponding to the onset of plastic flow (44 000 ± 4000 atm) and the phase transformation (114 000–122 000 atm at 160°C). The values obtained for the phase transition in germanium by the dynamic method differ to a smaller extent from the results

of static studies carried out by various investigators than they differ from one another [78,84].

Static [78,85] and dynamic [12] data for silicon are similar to those for germanium. The Hugoniot curve for this element also shows two breaks, the first corresponding, as in germanium, to the onset of plastic flow and the second to a polymorphic transformation.

Fig. 4 presents the phase diagram for metallic bismuth [86,87], the points corresponding to the breaks in the Hugoniot curve for bismuth specimens subjected to preliminary heating or cooling being indicated [88]. The breaks in the Hugoniot curve for bismuth evidently correspond to the bismuth I–bismuth III transition. The region of stability of the bismuth II phase, located between them, is so narrow that it is not reflected in the dynamic curve. The fact that the point x is in the region of stability of the liquid phase appears so far incomprehensible. On the whole, the agreement between dynamic and static experiments on bismuth may be regarded as satisfactory.

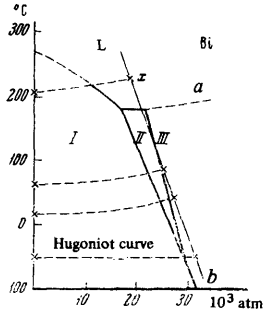

Figure 4. Phase diagram for metallic bismuth and data obtained in dynamic experiments; *a*) Refs.86 and 87; *b*) Ref.88.

However, the agreement between static and dynamic studies is not always as good as this. For example the Hugoniot curve for graphite, treated, following Alder and Christian [2], as corresponding to the transformation of graphite into diamond, occurs at a pressure of the order of 200 000 atm and a temperature of about 300°C, while the P–T diagram for carbon [78] (Fig. 5) does not show any phase equilibrium lines in this region. If it is assumed that the agreement between static and dynamic studies must be always satisfactory, then the transition may be attributed only to metastable fusion of graphite. However, so far there are no data confirming such a view.

A similar situation is observed also in the analogue of crystalline carbon–boron nitride. According to Bundy [89], the dense modifications of boron nitride (borazon) become stable at comparatively low pressures (not greater than 40 000 atm). However, our data on the shock compressibility of the graphite-like boron nitride [21] show that under dynamic conditions the phase transition begins at only about 130 000 atm, although the temperature does not then exceed 200–300°C. On the other hand, according to the indirect data obtained by Bundy [89], unstable fusion occurs at very much higher pressures. However, it should be noted that, when boron nitride specimens subjected to shock-wave compression are preserved, the formation of the hexagonal wurtzite-like variety of borazon is observed and not the cubic sphalerite-like modification. The region of stability of the former modification in the phase diagram for boron nitride and the corresponding phase-equilibrium lines have not been elucidated hitherto. One cannot exclude the possibility that the break in the Hugoniot curve is associated with the phase-equilibrium line of precisely this modification.

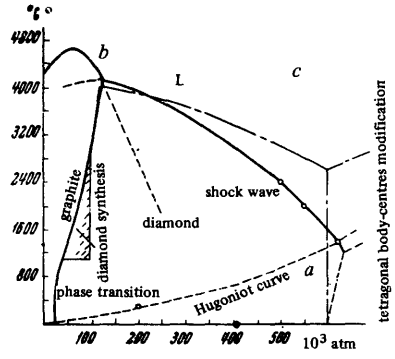

Figure 5. Phase diagram for carbon and data obtained in dynamic experiments: *a*) Ref.2; *b*) Ref.78.
* Tentative interpretation (Ed. of Translation).

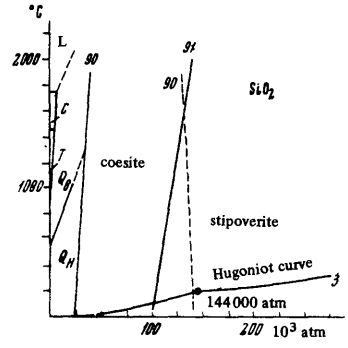

Figure 6. Phase diagram for silica and data obtained in dynamic experiments [3,90,91] (the numerals against the curves denote literature references).

The question of whether or not dynamic and static studies on crystalline quartz are comparable has not been inadequately elucidated. On the one hand, it follows from the work of Wackerle [3] that the latter observed a phase transition at 144 000 atm under dynamic conditions. The temperature (about 200°C) and pressure of this transition lie satisfactorily on the coesite–stishovite phase-equilibrium curve determined in Boyd's experiments [90], but differ markedly from the static experiment of Stishov [91] (Fig. 6). At the same time the point of intersection of Wackerle's Hugoniot curve [3] with the coesite–stishovite phase-equilibrium line obtained by Stishov [91] corresponds satisfactorily to the first break in the compressibility curve for vitreous silica obtained in Wackerle's dynamic experiments. On the other hand, Adadurov et al. [4], who used the method of dynamic volume compression ("method of mixtures") [92], showed that the phase transformation under these experimental conditions begins only at 200 000 atm,

but no phase-equilibrium lines are found in this region of the phase diagram for silica.

Although the possibility of achieving both chemical and phase transformations is determined by the thermodynamic background, it is probable that significant deviations from results expected on thermodynamic grounds may also occur due to the peculiarities of shock-wave compression. Here we have in view both the enormous rates of application of the load (small width of the shock-wave front) and the high rates of removal of the load (the duration of application of high pressures to the substance).

As already stated, plastic flow in shock-waves accelerates various transformations but does not make them infinitely fast. Under favourable conditions the transformation can occur immediately beyond the intersection of the Hugoniot curve and the corresponding phase-equilibrium line on the P–T diagram. However, it should be noted that the transformation induced by the shock wave can begin also at much higher pressures than the pressure corresponding to the above point of intersection. This can be due to at least two factors. On the one hand, the dynamic yield point can exceed the pressure indicated by the phase diagram, and, until this yield point is passed, the compression remains monoaxial and the mobility of atoms is insufficient for a change in their coordination environment during short periods. Possibly the characteristic features of the shock-wave compression of crystalline quartz and the absence of breaks in the compressibility curves in the region of the quartz–coesite equilibrium are due precisely to the exceptionally high yield point of both crystalline and vitreous quartz (the dynamic yield point of crystalline quartz is 35 000–60 000 atm along the x axis, 65 000–80 000 atm along the z axis, and 98 000 atm for fused quartz [3]). On the other hand, one cannot exclude cases where, despite a vigorous plastic flow, the duration of the transformation is nevertheless fairly high and there is not sufficient time for the process to occur in the shock wave. Here there may be two cases. If the relaxation time falls with increasing pressure, then at a sufficiently high shock pressure there may come a moment when there is sufficient time for the transformation to occur in the shock wave and we obtain results differing significantly from static experiments, i.e. higher pressures. The characteristic features of the shock-wave compression of graphite and boron nitride can be fully accounted for by the effect of this factor. On the other hand if the relaxation time increases with impact pressure, then the transformation cannot be achieved at all.

Polycrystalline or powdered materials rather than single crystals are most frequently investigated by dynamic methods, particularly in experiments with recovery of the specimen. In such cases it should be borne in mind that pressures significantly exceeding the average pressure which obtains in the specimen after all the pores have been closed up inevitably arise in microregions. This local excess pressure may give rise to local thermodynamic conditions suitable for the transformations, although the average pressure in the specimen is still much lower than would be required in accordance with the phase diagram.

The irreversibility of the processes occurring in the shock wave is determined not only by the phase diagram but also by kinetic factors, in the first place the characteristic features of the removal of shock-wave load. The removal of load during the passage of the rarefaction wave occurs much more slowly than the generation of high pressures and temperatures in the application of the shock-wave load to the substance and there is then no random mobility of the atoms. However, the time of removal of pressure is still smaller by a factor of many powers of ten than can be achieved in static experiments. Since the removal of load is adiabatic, just as rapid a fall of temperature is observed simultaneously. As a result, it is possible to quench the high-pressure phases, provided of course that they are capable of metastable existence at the residual temperatures which obtain after the passage of the shock wave. If the residual temperatures are fairly high, the phases formed at high pressures (metastable under normal conditions) may be annealed. Thus, despite the fact that Hugoniot curves indicate virtually complete conversion of graphite into diamond on shock-wave compression, the temperatures in the recovered specimens are so high that the diamond formed is almost completely reconverted into graphite. On the other hand, we have already mentioned that in many cases there is so far no direct evidence of the occurrence of processes in the shock wave itself during the application of high pressures. One cannot exclude the possibility that many processes occur exclusively due to the residual temperatures. A good example of this may be the present authors' investigation of the behaviour of antimony oxides, which decompose until the liberation of metallic antimony when the specimens are kept in iron tubes but remain virtually unchanged when copper tubes are used. In the first case the appearance of metallic antimony is entirely due to the interaction of the oxides with the material of the tube walls.

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Shock-wave compression of condensed systems makes it possible to achieve a number of chemical and phase transformations in unusually short times. The pressures set up by shock waves are at present unattainable in static apparatus. Furthermore, shock waves can also affect the substances to which they are applied as a result of very high temperatures (up to tens of thousands of degrees in the shock wave and up to several thousand degrees after the passage of the expansion waves).

The possibility of applying such high pressures and temperatures to matter arose in chemical investigations only in recent years. As in any new field of study, so far the number of problems and puzzling phenomena is much greater than the available answers. Only the first steps have been taken to bring into closer correspondence and make more consistent the dynamic and static experiments and to elucidate the mechanism of the processes occurring in the shock wave.

However, it is quite clear that the elucidation of the laws governing the reactions in shock waves would not only provide experimenters with the means of obtaining thermodynamic parameters in those regions of temperature and pressure which will remain unattainable by other methods in the forseeable future, or a method whereby it will be possible to influence radically the kinetics of many processes, but also it will provide the means for a significant modification of the properties of many substances and their preparation in new, previously unknown forms. Further development of experimental methods for the recovery of substances on removal of the high pressures associated with shock-wave compression and the theoretical study of this aspect of the problem will play a special role in this.

Until recently the sole aim of deformation was destruction. The development of studies on the effect of shock waves on matter will make it possible to consider the application in synthetic chemistry of the energy of powerful explosions, including nuclear explosions.

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Application of Electrical Spin Resonance in Chemical Kinetics

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The application of electron spin resonance (ESR) in the study of the kinetics of chemical reactions involving free radicals and paramagnetic ions is a very promising and rapidly developing field of study. In the first part of the review certain theoretical aspects and latest advances in studies on the kinetics of chemical reactions by the ESR method are discussed. Particular attention has been given to methods of analysis of the ESR spectra of free radicals, to methods for the calculation of concentrations, and also to a new method for the determination of local concentrations of paramagnetic centres from the dipole-dipole contribution to ESR line width.
In the second part of the review examples of the application of electron spin resonance in chemical kinetics are examined, and studies on radical reactions and the cage effect in solid matrices, and also measurements of steady-state concentrations of active radicals directly in the course of chemical reactions are discussed in detail.

CONTENTS

I. Introduction	402
II. Analysis of ESR spectra	403
1. Determination of average absolute concentrations	403
2. Measurement of local concentrations of paramagnetic centres	405
3. Formal mathematical analysis of ESR spectra	407
4. Quantum-chemical analysis of ESR spectra	409
III. Study of the kinetics and mechanism of chemical reactions by the ESR method	409
1. Gas-phase reactions	409
2. Liquid-phase reactions	410
3. Reactions in solids	413

I. INTRODUCTION

This review was written on the suggestion of the late V. V. Voevodskii, one of the first scientists to understand the exceptionally great promise of the application of electron spin resonance in chemical studies. Thanks to him, Soviet science now occupies a leading place in the field of chemical ESR spectroscopy.

The application of radiospectroscopic methods, nuclear magnetic resonance (NMR), and electron spin resonance (ESR) led to significant advances in studies on the fundamental problems of theoretical and applied chemistry. Radiofrequency techniques enable often hitherto unobtainable information about the structure of matter and the dynamics of the processes occurring in it to be obtained. In particular, electron spin resonance

permits the observation of signals (arising as a result of the absorption of energy on transitions between Zeeman sublevels) from unpaired electrons; the actual carriers of such electrons may be a wide variety of paramagnetic centres (PC)—atoms, molecular fragments (free radicals), molecular ions, individual paramagnetic ions, solid-state defects, molecules in the triplet state, etc. On the other hand, real chemical processes usually take place via a series of fundamental intermediate stages, with participation of chemically active valence-unsaturated species—radicals, ions, etc. Thus the ESR method is, as it were, specially suitable for the study of the mechanism of chemical reactions, because such study in fact consists in the identification and quantitative investigation of the sum total of intermediate processes.

One of the valuable features of the ESR method is the fundamental ease of the quantitative measurement of the effect: in the absence of saturation, the total intensity of the absorption lines is proportional to the number of absorbing species, the spectroscopic absorption coefficients being the same for the majority of paramagnetic centres. Furthermore, the ESR method is sensitive only to paramagnetic centres, regardless of the remaining species in the system, which leads to high sensitivity of the method, permitting the detection of paramagnetic centres at concentrations of 10^{-10}–10^{-11} M. However, the value of the ESR method does not lie solely in the quantitative detection of signals from paramagnetic centres. The interaction of an unpaired electron with paramagnetic nuclei and neighbouring electrons and the dependence of these interactions on the geometry of the species and internal motions are all reflected in the ESR spectrum in the form of a hyperfine structure (HFS), fine structure, line broadening due to relaxation, displacement of the positions of the lines, etc. The physical principles of electron spin resonance and nuclear magnetic resonance are now widely known and it is therefore unnecessary to dwell on these problems. The above features of the ESR spectrum permit an approach to the determination of the true structures of complex paramagnetic centres, the details of their geometry, the distribution of unpaired electron density among various functional groups, and can even provide information about the interaction of the paramagnetic centres with the surrounding medium and the internal motions in the medium.

Nowadays several dozen papers on the study of chemical problems by the ESR method are published every month. The ESR method is used in a wide variety of chemical fields—organic chemistry, electrochemistry, radiation chemistry, polymer chemistry, quantum chemistry, chemical kinetics, and catalysis. It would clearly be unreasonable to attempt to describe all the aspects of the chemical applications of electron spin resonance. However there is one problem which combines all the studies in this field—the problem of the extraction of "chemical" information from ESR spectra. With the existing experimental techniques, it is relatively easy to detect the ESR spectra of a wide variety of chemical systems, but it is much more difficult to interpret correctly these spectra and to obtain from them the chemical information concealed in the various features of the hyperfine structure and the line form of the signal. Certain fundamental problems of the analysis of ESR spectra from the standpoint of obtaining "chemical" information will therefore be discussed in the first part of the review.

In the second part the use of electron spin resonance to study the kinetics and mechanism of chemical reactions will be mainly examined. The use of electron spin resonance in the investigation of the kinetics and mechanism of reactions is one of the most important and most interesting aspects of the application of this method.

Chemical applications of electron spin resonance outside the scope of this theme can be roughly characterised as structural–chemical studies. A much larger number of reviews and monographs have been devoted in recent years to these investigations than to studies on the kinetics and mechanism of reactions.

II. ANALYSIS OF ESR SPECTRA

In chemistry, the analysis of ESR spectra should usually provide an answer to the following questions[1]: (1) what paramagnetic centres are formed under particular conditions; (2) what is the concentration of these centres and how does it vary under different conditions; (3) what is the distribution of spin density of the unpaired electron in the active centre; (4) in what way does the unpaired electron interact with the surrounding medium, etc.

In order to calculate the concentration of paramagnetic centres, it is necessary to calculate the area under the absorption curve and to compare it with the area under the signal from a standard (with a known number of paramagnetic centres). Such standard signals may be provided by stable radicals (diphenylpicrylhydrazyl, diphenylnitric oxide, etc.) and ions [manganese(II) compounds, $CuCl_2.2H_2O$ crystals, etc.] Here the most difficult problem is the calculation of the area and, in some cases, the evaluation of the absorption coefficient.

To obtain an answer to the remaining questions, it is in general necessary to perform an analysis in two consecutive stages—formal mathematical and then quantum-chemical analysis of the spectrum. In the first stage one must establish from the experimental spectrum, which may consist of a large number of weakly resolved lines, which interaction determines the formal spectrum, i.e. one must usually establish with which nuclei the unpaired electron reacts, what are the interaction constants, line widths, etc.

In the second stage, using quantum-chemical relations, it is possible to establish the structure of the radical, the distribution of spin density, and the nature of the motion of certain functional groups. There is an extensive literature on this question, including reviews and textbooks, and therefore it will be considered only briefly. The problems of the formal mathematical analysis of the spectra will be discussed in greater detail. Although the creation of effective methods for the mathematical analysis of complex ESR spectra is absolutely essential for the successful application of this method, detailed studies of the problems of formal mathematical analysis developed only very recently.

1. Determination of Average Absolute Concentrations

In principle this is a simple problem. The integral intensity of the ESR signal is proportional to the number of paramagnetic centres, consequently in the simplest case, when there is a standard with a known number of unpaired electrons N_{st}, we have

$$N_{sp} = N_{st}\frac{S_{sp}}{S_{st}},$$

where S_{sp} and S_{st} are the areas under the ESR absorption curves for the specimen and the standard respectively. Since the signal is usually recorded in a differential form,

the calculation requires graphical integration. One can use the relation

$$S = \int_{-\infty}^{\infty} I(x)\,dx = \Big|_{-\infty}^{\infty} xI(x) - \int_{-\infty}^{\infty} xI'(x)\,dx\,. \qquad (1)$$

Since the first term on the right-hand side of Eqn. (1) is zero both for the Lorentzian and Gaussian line forms, Eqn. (1) permits the replacement of double integration by a single determination of the first moment of the spectral line.

The last operation was further facilitated[2] by the introduction of nomograms consisting of a family of hyperbolae $xI' = C_i$. After the superposition of the nomograms on the spectrum, the integration reduces to adding together the values of C_i corresponding to the experimental curve (see Fig. 1). The accuracy of such treatment is 20–30%,

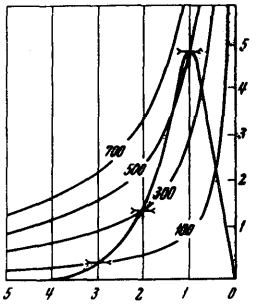


Figure 1. Diagram illustrating the use of a nomogram for the calculation of the first moment of the ESR line[2]; $S = 2(100 + 300 + 500) = 1800$ arbitrary units.

as in graphical integration. It is then found[3] that the integration step Δx should not be made too small, a sufficient condition is $\Delta x < \frac{1}{2}\Delta H_u$. The blurring of the hyperfine structure due to modulation is not reflected in the value of S. Furthermore, S does not depend in principle on the starting point of the calculation (but the accuracy is greater if the starting point of the calculation coincides with the true centre of the spectrum). However, the greatest error can be introduced by the superposition of a "parasitic" line due to the drift of the zero or due to the presence of a paramagnetic background. To take this superposition into account it is necessary to recover the background line, to determine the first moment for the latter, and to subtract the result from $M_{1\,\mathrm{exp}}$. If it is assumed that the zero shift is linear, then it is easy to show that

$$M_{1\,\mathrm{drift}} = 2\int_0^{\infty} \frac{\Delta I_0'}{2\Delta H_0}\,HdH = \frac{1}{3}\Delta I_0'(\Delta H_0)^2$$

and

$$S = M_{1\,\mathrm{exp}} - \frac{1}{3}(\Delta H_0)^2\,\Delta I_0'\,,$$

where ΔH_0 is the distance from the zero line to the last point of the integration and $\Delta I_0'$ is the total zero shift (see Fig. 2). In some cases one can determine the area more simply from the formula

$$S = \alpha\varkappa\Delta H_{\frac{1}{2}}^2 I_m'$$

where $\alpha = \Sigma A_i/A_m$ (A_i are the intensities of the hyperfine structure components) and the line form coefficient is

$$\varkappa = \begin{cases} \pi/\sqrt{3} & \text{for Lorentz line form} \\ \frac{1}{4}\sqrt{\frac{\pi e}{2}} & \text{for the Gaussian line form.} \end{cases}$$

Since the form and width of an individual line are not usually evident, the empirical coefficient is preferred:

$$\varkappa_{\mathrm{eff}} = S/I_m'\,. \qquad (2)$$

When a large series of measurements is made, one can determine κ_{eff} at only a few reference points and at the remaining points the area S can be measured on the basis of I_m' and the value of κ_{eff} interpolated for the given point (see Fig. 3).

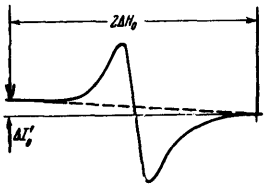


Figure 2. Diagram illustrating how the shift of the zero line is taken into account in the calculation of the first moment.

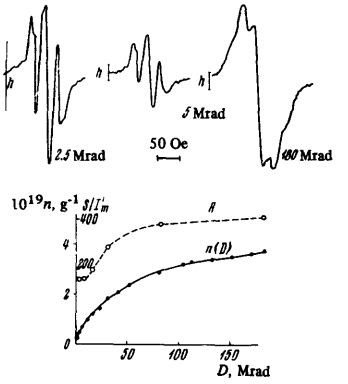


Figure 3. An example of the construction of the kinetic curve on the basis of ESR data (kinetics of the accumulation of free radicals in the low-temperature β-radiolysis of glycine); A—calibration curve for the determination of the ESR line form coefficient.

Additional difficulties arise when the standard and the specimen differ in the effective spin S, temperature, g-factor, etc. The spin and temperature can be easily taken into account, since

$$S \sim N\,\frac{S(S+1)}{T}\,.$$

When there is a considerable difference between the g-factors, it is necessary to take into account the difference between the probabilities of the transition.

We shall now discuss two examples, which are important in practice, of the calculation of the absolute concentrations of paramagnetic centres for which the absorption

coefficients differ significantly from the coefficients for the free spins. The existing theoretical formulae for signals from triplet molecules with $g = 4(\Delta M_S = 2)$ are complex and inaccurate. Alfimov et al.[4] proposed a novel method for the determination of the number of triplet centres based on recording by the ESR method the time of the increase and fall of the intensity of the signals from the triplets. On the basis of the simplest kinetic mechanism,

$$M_0 \xrightarrow{\beta j} M_\tau ,$$
$$M_\tau \xrightarrow{1/\tau} M_0 ,$$

the curve for the accumulation of triplets under the action of a beam of electrons with an intensity j is given by

$$N_\tau = N_0 \frac{\beta j}{\beta j + 1/\tau} \{1 - \exp[-(\beta j + 1/\tau) t]\} \qquad (3)$$

and, after the beam is switched off, the steady-state concentration becomes

$$(N_\tau)_{cr} = \frac{\beta j N_0}{\beta j + 1/\tau} .$$

From Eqn. (3), the time constant for the accumulation of triplets is

$$\tau_a = \frac{1}{\beta j + 1/\tau} .$$

On eliminating βj from the last two equations, we obtain

$$(N_\tau)_{st} = N_0 \left(1 - \frac{\tau_a}{\tau}\right) .$$

Finally specific difficulties arise in the identification and determination of the concentrations of free atoms (except H atoms) and radicals in the gas phase. Here, in contrast to a condensed phase, the orbital motion of the electrons may not be frozen and therefore the g-factors and spectroscopic absorption coefficients are significantly smaller and larger than for the condensed phase and vary from species to species. Furthermore, the spectra of di- and poly-atomic radicals show a rotational structure which leads to a very complex system of ESR lines, spreading over a range of several kilo-oersteds; however, as a rule it is possible to record only part of these lines. In this connection, the determination of the absolute concentrations of species in the gas phase requires special calculations every time. The first such calculation, the aim of which was to calibrate O against O_2, was performed by Krongebb and Strenberg[5]. Later calibration calculations for OH against NO and for halogen atoms against O_2 were performed independently by Nalbandyan et al.[6] and by Westenberg[7]. In such calculations account is taken of the fact that the absorption in OH, NO, etc. is due to electric dipole transitions. The resonator is usually completely filled with the gas, so that the paramagnetic OH species come within the region of the antinode of the electric field and the NO used as standard permits automatic allowance for the effect of the configuration of the fields. However, if the measurements are made at high temperatures, considerable temperature differences always appear in the resonator, and nitric oxide cannot be used, since its signal depends markedly on temperature. In these cases Nalbandyan and coworkers[6] use molecular oxygen as an intermediate standard.

2. Measurement of Local Concentrations of Paramagnetic Centres

The methods for the determination of the number of paramagnetic centres by the ESR method have already been examined. On dividing this number by the volume of the specimen, we can always determine the average concentration of paramagnetic centres in the specimen. However, this quantity can be usefully employed in physicochemical calculations only when it is certain that the distribution of paramagnetic centres throughout the volume is uniform (equally probable). If we are dealing with a gas or liquid phase, such a problem does not arise—here the distribution of all the active centres is homogeneous. However, in a solid phase and in heterogeneous svstems it is easv to imagine a non-uniform distribution of paramagnetic centres —such non-uniformities can arise from radiation tracks on irradiation, phase separation on freezing, active sites on the surface, etc. Here the study of the intensity of the signal is of no avail and it is necessary to seek other ways of estimating the true density of paramagnetic centres. In principle, one can use the fact that, at the concentrations usually recorded by the ESR method, the average distance between paramagnetic centres is such that their dipole–dipole interaction should influence the form of the spectrum (0.1–1 Oe). According to fairly simple calculations[8,9], there is a relation between the dipole–dipole contribution to line width between the points of maximum slope and the concentration of paramagnetic centres (for $n < 1\%$, which is always the case in chemical studies):

$$\Delta H_i(\text{Oe}) = Bn \ (\text{cm}^{-3}), \qquad (4)$$

where

$$B = \begin{cases} 5.4 \times 10^{-20} \text{ Oe cm}^3 \text{ (random distribution, Lorentz line form)} \\ 4.9 \times 10^{-20} \text{ Oe cm}^3 \text{ (uniform distribution, Gaussian line form).} \end{cases}$$

If this interaction determines the apparent line width, the problem may be regarded as solved. Wyard[9] observed directly in irradiated frozen solutions of hydrogen peroxide the variation of line width with concentration (i.e. the area of the signal). According to his estimate[9], $B = 7.5 \times 10^{-20}$ Oe cm^{-3}. In this case the ESR signal consists of a single line. For complex ESR spectra the detection of line broadening appeared at first to be a hopeless task, but thorough analysis of the accumulation curve recorded up to large doses enabled the present author together with Mikhailov[10] to detect the broadening of the hyperfine structure components at average concentrations of the order of 10^{19} cm^{-3} (Fig. 4). The quantity $\sqrt{\kappa_{\text{eff}}}$, where the line form coefficient κ_{eff} was determined from Eqn. (2), served as a measure of the width ΔH_i of an individual component. For complex spectra, this method proved to be more sensitive than the direct measurement of line width or the calculation of the second moment. The undefined multiplier in the formula $\Delta H_i = \beta\sqrt{\kappa}$ was determined for the most highly resolved signal with the aid of the "Atlas of ESR Spectra". Fig. 4 shows that ΔH_i increases linearly with the average concentration n (this can be regarded as proof of the dominant contribution of spin–spin interaction to ΔH_i), and n_{loc} exceeds n significantly but increases together with the latter. Thus here the hyperfine structure components are homogeneous. In the most complex case of non-homogeneous lines, consisting of a large number of unresolved spin packets, ΔH_i in Eqn. (4) must be replaced by the width of the spin packet ΔH_S. The relaxation characteristics of the ESR signal obtained by the spin-echo or successive saturation methods have begun to be used recently for the determination of ΔH_S.

The application of the spin-echo method (based on Hann's principle[11,12]) in the study of free radicals in solid matrices was first described by Raitsimiring et al.[13] Despite certain theoretical difficulties in the interpretation of the experimental data, this method is extremely promising.

In particular, it is also evident from the results of Raitsimiring et al.[13] that the local radical concentration measured from ΔH_S increases in parallel with the average concentration, remaining higher than the latter in a number of cases.

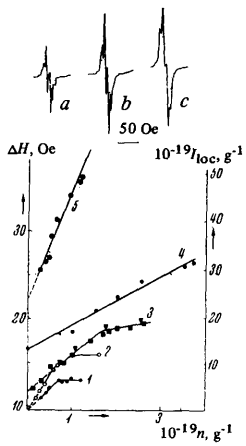


Figure 4. Variation of the width of the hyperfine structure components of the ESR spectra of irradiated substances with the average concentration (i.e. radiation dose):
1) cytidine; *2*) guanosine; *3*) thymine; *4*) glycine; *5*) DNA.

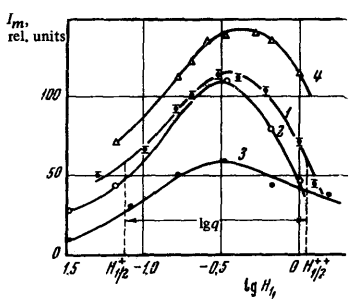


Figure 5. Example of the analysis of microwave saturation curves; variation of the intensity of the ESR signal in irradiated substances with the power of microwave detector[14] (77°K):
1) α-alanine; *2*) guanine hydrochloride; *3*) phenol; *4*) glycine.

The present author initiated a simpler (but less sensitive) method for estimating ΔH_S from the width of microwave saturation curve[14] based on the theory of inhomogeneous saturation of Portis[15] and Castner[16]. Some of the results[14] are presented in Fig. 5. At saturation the homogeneous line broadens because its centre is saturated to a greater extent than the edges, so that, when the power applied is high, the intensity of the signal falls to zero. If the effective width of an inhomogeneous line $\Delta H^* \gg \Delta H_S$, an increase of ΔH_S will not affect ΔH^* and the intensity of the signal will cease to depend on the amplitude of the microwave field H_1, i.e. the width lg$q$ of the $I'_m - \lg H_1$ saturation curve becomes infinite. Theoretical calculation of saturation curves for various $\Delta H^*/\Delta H_S$ makes it possible to plot a calibration curve: $\Delta H^*/\Delta H_S = f(q)$. Such a calculation has been performed by Castner[15] and then used for estimating ΔH_S.[17,18] However, Castner's calculation[15] was made for an ESR spectrometer without magnetic modulation and this was not stated. Zhidkov et al.[14] carried out the calculation for the usual experimental conditions (modulation of the magnetic field with an amplitude $\Delta H_S \leq \Delta H_M < \Delta H^*$; in view of the slow-pass conditions obtaining the modulation frequency $\nu_M \ll 1/T_1$; in the experiments[14] $\nu_M = 333$Hz). Then for $q < 50$ the calibration relation is described by an almost linear function

$$\frac{\Delta H^*}{\Delta H_S} \simeq 0.72\,q - 6.15\,,$$

In the experiments, apart from the cases where $n_{loc} \gg n$, the equality $n_{loc} \simeq n_{av}$ was obtained for certain specimens, which may be regarded as confirmation of the validity of the calculation. In the general case the theoretical interpretation of continuous saturation curves is also quite difficult, since the calculations were made on the assumption of non-interacting spin packets (i.e. the absence of spectral diffusion) and without taking into account the contribution of exchange interaction. (It has now been shown that at concentrations less than 10^{20} cm^{-3} the exchange contribution to line width may be disregarded).

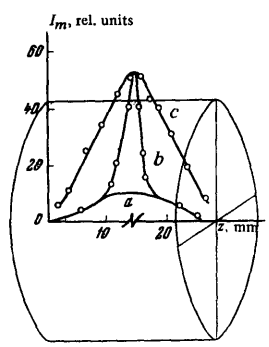


Figure 6. Distribution of sensitivity in an ESR resonator:
a) in the normal case; *b*) in a resonator with a spiral nozzle;
c) in a resonator with mobile packing[19].

In connection with the measurement of the concentrations, it is interesting to consider briefly also the following problem. The microwave resonator usually consists of a "transducer" with a linear dimension of about 30 mm (X-range) or 8 mm (K-range) and therefore if the measurements are on an extended volume (paramagnetic centres in a jet, in a gas mixture, etc.), we can determine only the concentration averaged over the resonator. We believe that an interesting possibility for the determination of local concentrations at a "point" with dimension smaller by a factor of 10 than that of the resonator arises from the effect, observed by the present author together with Taranukha, involving the localisation of the microwave power by a spiral section[19]. It was found that, when one or two turns of a conducting spiral are placed along the antinode of the lines of force H_1, then it is possible to obtain at the location of the spiral a δ-flash of microwave power, so that the instrument begins to "see" virtually only whatever is located in the zone of its spiral (see Fig. 6). Measurements on model objects confirmed this possibility, but a very unfavourable feature of this system is the necessity for a spiral of very small diameter (1–2 mm for a 3 cm resonator).

3. Formal Mathematical Analysis of ESR Spectra

The ESR spectrum is a system of lines, the derivation of chemical information from which constitutes a special task. For chemically active species (free radicals) the complexity of the spectrum is usually due to the hyperfine structure (i.e. the interaction of the unpaired electron with the nearest paramagnetic nuclei) and also the anisotropy of the hyperfine structure and the positions (g-factor) of the lines. Two stages are required for the identification of the paramagnetic centres: (1) one must establish with which nuclei (and with what constants) the unpaired electron interacts; (2) on the basis of the findings in the first stage, one must establish, using the methods of quantum chemistry, the chemical structure of the paramagnetic centre and, as far as possible, its geometrical structure and the distribution of the spin density of the unpaired electron.

We shall consider initially a spectrum consisting of well—resolved lines (i.e. line width $\Delta H_i < a_{\min}$). This spectrum must correspond to a system of levels (under the conditions of a strong field):

$$\Delta E = g\beta H + \sum_k a_k I_{z_k} \ ,$$

where a_k are hyperfine structure constants and I_{zk} the projections of the nuclear spins.

As a result of the interaction of the unpaired electron with the kth nucleus, $2I_k + 1$ lines are produced, and if there are N nuclei, the number of lines is $\prod_{k=1}^{N} (2I_k + 1)$. These lines are distributed in such a way that the distances from the extreme line to the others are a_1, a_2, a_3, ...; $a_1 + a_2$, $a_2 + a_3$ ...; $a_1 + a_2 + a_3$, ... etc. (see Fig. 7).

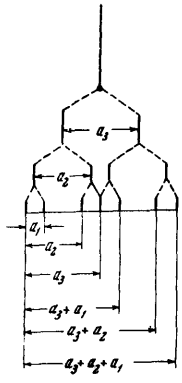


Figure 7. Diagram illustrating the formation of the hyperfine structure (splitting by three protons with $a_1 : a_2 : a_3 = 1 : 3 : 4$).

Therefore it is readily seen that the hyperfine structure of the ESR spectrum can be represented by the polynomial

$$\prod_{k=1}^{k_m} (1 + z^{\alpha_k})^{S_k} \quad \text{for } I = 1/2$$

$$\prod_{l=1}^{l_m} (1 + z^{\alpha_l} + z^{2\alpha_l})^{S_l} \quad \text{for } I = 1 \text{ etc.}$$

where α_k represents the different splittings measured in relative units ($\alpha_k = a_k/a_{\min}$) and S_k the number of nuclei for which $a = a_k$, i.e. the multiplicity of the degeneracy. After carrying out the multiplication, we obtain a polynomial $\Sigma A_m z^m$, in which the coefficients A_m correspond to the relative line intensities (the multiplicity of the degeneracy) and the exponents to their distances from the first left-hand line in units of $a_{\min}$. In particular, for n equivalent protons the characteristic polynomial is $(1 + z)^n$, which corresponds to $n + 1$ lines with a binomial distribution of intensities. Such formalised representation of the hyperfine structure makes it possible to formulate the problem of the analysis of the spectrum. The polynomial $\Sigma A_m z^m$ is known from experiments. The problem is how to recover from it the initial product. We shall examine, for simplicity, only nuclei with $I = 1/2$. The total number of lines is 2^N, where N is the number of nuclei, and therefore

$$N = \log_2 \frac{\Sigma A_i}{A_0} \ .$$

It is then clear from the structure of the characteristic polynomial that $A_1/A_0 = S_1$, the number of nuclei with minimum splitting. Finally the ratio of the total splitting in the spectrum to the smallest is

$$\frac{a^*}{a_{\min}} = \sum_{k=1}^{k_m} \alpha_k S_k \ .$$

In spectra corresponding to not more than two groups of non-equivalent nuclei, the number of these relations is sufficient for the determination of all the α_k and S_k. In the general case Dobryakov[20] obtained recurrent relations, from which all the α_k and S_k can be found from specified A_m. Thus the problem can be regarded as solved in principle (for $I = 1/2$), but since A_1 and a_1 (the intensity of the weakest component and the minimum splitting) enter into all the formulae, the above analysis is applicable only to relatively rarely encountered ideal "line" spectra.

Real spectra, particularly those of condensed phases, usually have line widths comparable to (or greater than) the minimum splitting. The method of trial and error has been used for a long time to analyse such spectra—a spectrum with a given structure is constructed taking into account the finite width and form (Lorentzian or Gaussian) of the individual line and the resulting curve is compared with experiment; when there is agreement, the theoretical spectrum yields a set of α_k and S_k values. Such construction is laborious and, in order to facilitate it, an atlas of theoretically calculated ESR spectra[21], containing a large set of spectra with various A_i and different resolutions ($\Delta H_i/a_{\min}$), was produced in 1962 at the Institute of Chemical Physics of the USSR Academy of Sciences. Experiments showed that the atlas causes the investigator to adopt fairly specific habitual procedures to interpret poorly resolved signals, but of course the atlas could embrace only a small part of line combinations encountered experimentally. At the present time there are specialised computers which can be used also for the synthesis of theoretical spectra. Finally the attempts to find the parameters of the theoretical spectrum by adjusting them on an electronic computer to fit the experimental spectra may be regarded as an improved version of the method of trial and error[22,23]. However, all this applies only to symmetrical multicomponent spectra, the description of which requires, apart from a set of S_k and α_k, the specification of only two parameters—$a_{\min}$ and ΔH_i. The line form due to the axial anisotropy of the g-factor is also described by only two parameters (Δg and H_i), and several studies have been devoted to the analysis of such lines[24-28].

In more complex cases where 3–4 or more parameters must be specified in order to describe the theoretical spectrum, the line form can be calculated only for definite sets of parameters specified *a priori*. Lefebvre and Maruani published recently a very complete programme for the computer calculation of spectra taking into account the splitting and the triaxial anisotropy of the g-factor and the hyperfine interaction[29]. The method of moments is also used for the analysis of poorly resolved ESR spectra[30]. However, the present author believes that the most logical formulation of the problem is analogous to that used by Dobryakov[20] for the analysis of line spectra. An attempt must be made to construct functional transformations, whereby the initial "physical" parameters of the spectrum can be found from its finite line form. It will be shown below on the simplest example that this can be done at least for spectra with a symmetrical hyperfine structure.

Let us examine the construction of the transformation, the reverse of the synthesis of the spectrum with a hyperfine structure, using a doublet as an example

$$F(x) = f(x+b) + f(x-b) \qquad (5)$$

where $b = \frac{1}{2}a_{\mathrm{H}}$. It is evident that

$$F(x+2b) = f(x+3b) + f(x+b)$$
$$F(x+4b) = f(x+5b) + f(x+3b),$$

where the left-hand side contains known functions. If we form an infinite series with alternating signs from $F(x+2kb)$, then all the terms on the right-hand side vanish except $f(x+b)$:

$$f(x+b) = \sum_{k=0}^{\infty} (-1)^k F(x+2kb). \qquad (6)$$

Thus, from the form of the envelope (apparent) of the lines, we can in principle find the form of the individual line (when b is known). The significance of transformation (6) can be readily elucidated from Fig. 8, which shows that, for sufficiently large k, the terms have virtually no effect on the pattern near $x = 0$. If b is unknown (and this is usually the case in the problem of spectral analysis), the following procedure can be used.

1. The right-hand side of Eqn. (6) is regarded as a function of x and b and preliminary differentiation of Eqn. (5) is carried out:

$$\Phi(x, y) = \sum_{k=0}^{\infty} (-1)^k F'(x+2ky).$$

Here y is a variable distance between the centres of the spectra and the terms of the summation have alternating signs. If $y = b$, then $\Phi(x, y) = f'(x+b)$. However, when $x = -b$, we have $\Phi(-b, b) = f'(0) = 0$ and therefore the function $\Phi(-y, y)$ has a remarkable property, namely it becomes zero when $y = b$. Hence it is possible to find b and then $f(x)$, i.e. to analyse the spectrum. This method of analysis was published by Newton et al.[31] The same method in principle was developed independently by Dobryakov and the present author[32], but in our version the analysis is carried out as follows.

2. It is clear from the scheme in Fig. 8*a* that, when the summation (5) is extended to $-\infty$, then along any section $0 \ldots y_0$ the modulus of the area under $\Phi(x, y_0)$ will become zero when $y = b$. Therefore we introduce the function

$$\psi_l(y) = \int_0^{ly} \left| \sum_{k=-\infty}^{\infty} (-1)^k F(x+2ky) \right| dx,$$

where l is an integral number which can be assumed to be 1 or 2 and the summation with respect to k can be carried out virtually from $-n$ to n, where $n \gg l$. This function becomes zero abruptly when $y = b$. Indeed, more rigorous treatment and model calculations showed[32] that, even for more complex cases, $\psi_l(y)$ is of the form shown in Fig. 8*b*, where a_N is the splitting of the nitrogen type, present in the spectrum of diphenylpicrylhydrazyl. Characteristic functions of a similar type can be constructed also for other values of I.

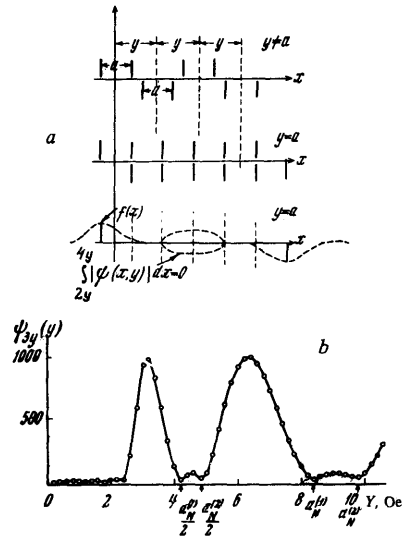


Figure 8. *a*) Diagram illustrating the analysis of a spectrum with a symmetrical hyperfine structure by the construction of the reverse transformation; *b*) analysis of the experimental spectrum of diphenylpicrylhydrazyl in dilute solution.

The method of Fourier transformations also opens up interesting possibilities for the analysis of ESR spectra[20,32]. Here the roots of the Fourier integral of the experimental function of line form are used to calculate the hyperfine structure constants.

The recently published "electronic" method for the sharpening of spectra by graphical differentiation or special magnetic modulation[33,34] and also of course the method of double electron–nuclear resonance[35] gives rise to specific possibilities in the analysis of poorly resolved spectra. However, all these procedures involve an appreciable loss of sensitivity in the recording of the signal.

In the identification of spectra the problem of how many different types of paramagnetic centres are responsible for the spectrum often arises. Generally, if the system of lines can be subdivided into a number of subsystems, each of which is consistent with the laws governing the formation of the hyperfine structure, then these systems can be logically attributed to different paramagnetic centres. However, for poorly resolved signals, it is difficult to arrive at any definite findings by this procedure. The method of microwave line saturation is more promising here (although it by no means always works). For example, when the system contains alkyl and peroxy-radicals, the signal from the first can be "suppressed" by high microwave power[36]. In general, for a quantitative separation of a two-component signal, it is sufficient to obtain two linear

sections on the saturation curve, since the slopes of these lines are proportional to $n_1 + n_2$ and n_2 respectively. Finally the change in line form on saturation may be regarded as qualitative evidence of the presence of more than a single signal. The point is that at saturation the form of the lines due to paramagnetic centres should either remain unchanged (inhomogeneous lines) or it should broaden symmetrically (narrow, almost homogeneous lines with $\Delta H_1 > \Delta H$). When it is certain that there is no impurity causing dispersion, asymmetric deformation of the spectrum is evidence of the superposition of two or several signals with different T_1 and T_2 and different g-factors[37]. †

4. Quantum-chemical Analysis of ESR Spectra

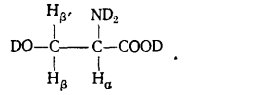
After formal mathematical analysis of the spectrum, we know in the general case all the constants of the magnetic interaction leading to the splitting or broadening of the ESR lines. Further analysis is based on the relations between the structure (electronic or geometrical) of the paramagnetic centres and the magnetic interaction obtained from the theory of ESR spectra. This theory has been described in detail in a number of monographs and reviews[1,38-43].

Only the following remarks need be made in addition to the data presented in the literature[1,38-43].

1. Refined effects involving changes in line form are increasingly used at the present time, after the publication of the elegant theoretical studies of Freed and Fraenkel[44], for the determination of the details of the electronic structure of radicals in liquid solutions[45].

2. When the g-factors are measured to within the 4th or 5th decimal place, they too can provide information about the chemical nature and the electronic structure of radicals. For example, Thomas[46] showed that peroxy-, hydroxy-, and alkyl radicals can be distinguished on the basis of the g-factors. Recently it has also been shown that the g-factor depends on temperature and the nature of the substituents in the radical[37,47].

We shall consider as a concluding example the "complete" analysis of the signal arising on γ-irradiation of α-substituted serine:



The spectrum, presented in Section III (Subsection 3) of this review, consists of 7 lines with the experimental intensities 12 : 16 : 21 : 31 : 25 : 18 : 20. The distances between the lines are approximately the same and equal to 13 Oe. The sum of the coefficients is

$$\frac{\Sigma A_m}{A_0} = \frac{143}{16} = 9 (= 3^2 \text{ or } 2^3),$$

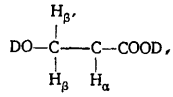
Since two nitrogen atoms cannot be present, it will be assumed that the hyperfine structure is due to three protons. Further,

$$\frac{A_2}{A_1} = \frac{18+16}{20+12} \simeq 1, \text{ i.e. } S_1 = 1; \; S_2 + S_3 = 2,$$

and therefore $S_1 = S_2 = S_3 = 1$. This means that the total splitting is

$$6 : 13 = 1 : 13 + (\alpha_2 + \alpha_3) \cdot 13 \text{ (oersteds)},$$

i.e. $\alpha_2 + \alpha_3 = 5$, so that $\alpha_2 \neq \alpha_3$. Hence $\alpha_2 = 2$ and $\alpha_3 = 3$. We conclude that the hyperfine structure is due to 3 non-equivalent protons with splittings of about 13.26 and 39 Oe. Such a situation can occur only in the radical



The splitting by the α-proton is evidently due to dipole–dipole nuclear spin interaction. For the β-splitting, we have $a_\beta \simeq 45 \rho_C^\pi \cos^2 \varphi$, and $\varphi_1 - \varphi_2 = <\text{HCH}$. With a favourable orientation, one of the β-splittings can reach 40 Oe, while the other should be small. Therefore it can be suggested that $a_\beta = 39$, $a_{\beta'} = 13$, and $a_\alpha = 26$ Oe. These figures are of course correct to within the line width and therefore the multiplicity of the splittings is only apparent. Next, with the aid of the Atlas[21], it is possible to obtain improved values of the constants: 40, 14, and 23 Oe respectively.

III. STUDY OF THE KINETICS AND MECHANISM OF CHEMICAL REACTIONS BY THE ESR METHOD

1. Gas-phase Reactions

The mechanism of gas-phase chemical reactions has been more thoroughly investigated than the mechanism of reactions in condensed phases. However, as regards the application of radiospectroscopic, methods the situation is reversed. This is probably because stable paramagnetic species do not exist in the gas phase (apart from the paramagnetic molecules of the type of O_2 and NO, which are not of particular chemical interest) and it is difficult to obtain high concentrations of active atoms and radicals. The ESR spectra recorded for H, O, S, K, Na, etc. atoms obtained in high-frequency discharges or by thermal dissociation are not themselves of significant interest to chemistry. A considerable advance took place after Voevodskii and coworkers[48] demonstrated the possibility of recording the ESR spectra of H atoms directly in the zone of a rarefied hydrogen flame in oxygen. According to Semenov and Hinshelwood's theory of branched-chain processes, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ proceeds at low pressures via the active centres H, O, and OH, which should give rise to an ESR signal. By drawing the flames from the combustion zone into the resonator, Voevodskii and coworkers[48] succeeded in recording considerable (up to 10^{15} cm^{-3}) concentrations of H atoms. Later these investigations were continued vigorously at the Institute of Chemical Kinetics and Geology [? tentative interpretation of abbreviation (Ed. of Translation)] of the Siberian Division of the USSR Academy of Sciences and at the Institute of Chemical Physics of the USSR Academy of Sciences, where V. N. Kondrat'ev and A. B. Nalbandyan and coworkers succeeded in recording, using a special cell, the signals from O and OH in the $H_2 + O_2$ flame and then also the signals from the active centres in a number of branched-chain combustion reactions: H, O, and OH in the $CO + O_2$ flame with small amounts of added H_2; O and SO in the $S + O_2$ flame and O in the $CS_2 + O_2$ flame; H, O, OH, and SO in the $H_2S + O_2$ flame[49,50]. The ESR spectra of H, O, and OH generated in the combustion of hydrogen in oxygen, obtained by Nalbandyan and coworkers[49], are presented as an example in Fig. 9*a*. Using the calibration method discussed earlier (with O_2 and NO), the absolute concentrations

† A more complete discussion of the methods of analysis of ESR spectra of free radicals is given by Dobryakov and Lebedev[32].

of the active centres in experiments with different jet velocities (i.e. different reaction times) were calculated from these spectra (Fig. 9*b*). The same Figure also presents the variation of the concentrations of H, O, and OH with reaction time calculated on a computer from the known kinetic constants; comparison of the experimental and theoretical curves constitutes very convincing confirmation of the existing theories concerning the mechanism of the process. By changing the initial values of the constants k_i in the calculations, it is possible to achieve complete agreement with experiment and thereby improve (or redetermine) the fundamental kinetic constants.

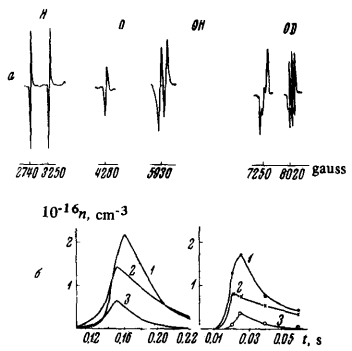


Figure 9. An example of the study of the mechanism of a gas-phase reaction—combustion of hydrogen in oxygen[49]: *a*) ESR spectra of active H, O, and OH centres; *b*) kinetic curves representing the variation of the concentration of the active centres with reaction time (comparison of the calculation with experiment); *1*) [O]; *2*) [H]; *3*) 10[OH].

However, the scope of the ESR method is not restricted to the confirmation and improvement of existing hypotheses. At the Institute of Chemical Physics of the USSR Academy of Sciences the ESR method has been used to justify certain new hypotheses of Semenov and Shilov concerning the role of chemical activation in branched-chain reactions[51]. Such a reaction should be a source of atomic concentrations (I and F) in excess of their equilibrium values. Indeed, by carrying out the reaction in the resonator, Shilov and coworkers[52] observed the spectra of atomic iodine (18 lines in the range between 3000 and 6300 Oe). The F and Cl signals were detected in the reaction between F_2 and C_2Cl_4 and the spectrum of atomic bromine was observed in the reaction between F_2 and CH_3Br.

No less interesting is the possibility of using ESR for the quantitative study of the fundamental stages of gas-phase reactions. Voevodskii and Panfilov[53] studied the reactions of atomic hydrogen with various hydrocarbons, by adding the latter to the $H_2 + O_2$ reaction zone and following the decrease of the intensity of the H signal as a function of the amount of additive and the extent of its combustion. This showed that, with rarefied flames, one hydrocarbon molecule can give rise to a chain of reactions involving the destruction of H atoms (from 2–3 for ethane to 75 for benzene). Nalbandyan and coworkers[54] established by the ESR method the pathway of the reaction between atomic oxygen and methanol:

$$O + CH_3OH \rightarrow \dot{O}H + \dot{C}H_2OH \quad \text{or} \quad \dot{O}H + \dot{C}H_3O \ .$$

For this purpose, they introduced CH_3OD or CD_3OH to $CO + O_2$ flames and determined the ratio [OD]/[OH] from the ESR signals. It was found that oxygen attacked mainly the methyl group.

Cold flames are not necessarily the only source of active species for the investigation of fundamental reactions. For example, Westenberg and coworkers in the USA made a quantitative study by the ESR method of the reaction of hydroxyl with OH, H_2, and CO, in which the very rapid reaction $H + NO_2 \rightarrow OH + NO$ served as a source of OH, and hydrogen was generated in the discharge[55]. In this investigation the rate constants for the reactions $OH + OH \rightarrow$, $OH + H_2 \rightarrow$, and $OH + CO \rightarrow$ at room temperature were determined with high accuracy and for the last two reactions the activation energies were also estimated (5.2 and 0.6 kcal mole^{-1}).

The active species produced in gas-phase reactions can be frozen out on cooled surfaces in order to accumulate them in high concentrations and to investigate in detail their ESR spectra. For example, by withdrawing atomic hydrogen from the discharge, it is possible to obtain phenyl radicals by the reaction[56]

$$H^{\cdot} + C_6H_6 \rightarrow H_2 + C_6H_5^{\cdot} \ .$$

The value of such preparations of radicals lies in the fact that their chemical structure is known *a priori* and the ESR spectra obtained can be used to identify the signals in other systems. A series of such radicals (propyl, butyl, heptyl, allyl, phenyl, and others) were obtained by Bennett and Thomas[57], with the aid of a technique involving a rotating cryostat and sodium beams, by the reaction

$$Na + RHal \rightarrow NaHal + R^{\cdot} \ .$$

The design of the experimental apparatus[57] is such that, by condensation of a third beam (in addition to RHal and Na), it is possible to study further reactions of the R$^{\cdot}$ radicals, for example:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \ ,$$
$$R^{\cdot} + C_2H_4 \rightarrow RCH_2CH_2^{\cdot} \ .$$

It was then found that oxygen reacts even at 77°K, while ethylene must be heated to 90–500°K. Bennett and Thomas[57] believe that, when account is taken of the gradual cooling of ethylene, it is possible to calculate the true rate constant for the reaction from the degree of conversion of R$^{\cdot}$ into $RCH_2CH_2^{\cdot}$ using an electronic computer. For example, they obtained in this way $E = 0.15$ kcal mole^{-1} for the reaction between C_6H_5 and C_2H_4. However, the accuracy of the determination of the constants by comparing the results of very cumbersome calculations with experiment is doubtful. Panfilov[58] applied the method involving the freezing out of the products from rarefied flames near the reaction zone in order to accumulate large amounts of free radicals. The sensitivity with respect to hydrogen atoms then increases at least by a factor of 50.

2. Liquid-phase Reactions

The paramagnetic centres (free radicals and radical-ions) in liquid and solid phases can have a wide variety of lifetimes, and henceforth we shall find it convenient to distinguish arbitrarily kinetically active and stable radicals. The application of electron spin resonance in chemistry began of course with the study of stable radicals and radical-ions. From stable radicals, interesting data were obtained on the electronic and geometrical structure, delocalisation of the unpaired electron, and internal motions

in molecules—data, which, as already stated, will not be discussed in great detail in the present review. From the standpoint of the kinetics and mechanism of chemical reactions, stable radicals as a rule do not behave as intermediate centres which can propagate real chemical reactions, but they can serve as models for the investigation of the most important problems of kinetics and reactivity. One of the first studies on the application of electron spin resonance in chemistry was the investigation of the rate of dissociation of hexaphenylethane into stable triphenylmethyl radicals, whereby it was possible to determine the heat of this reaction[59]. The capacity of stable radicals to recombine with active radicals makes it possible to follow the latter on the basis of the intensity of the ESR signal due to the stable radical. Diphenylpicrylhydrazyl is used particularly frequently as such a label. Buchachenko and others[39] investigated the kinetics of several hydrogen transfer reactions, such as the reaction between tri-t-butylphenoxyl and phenol, and determined the rate constant for the reactions and their dependence on the physical properties of the medium and the nature of the reacting molecules; these studies revealed a marked influence of hydrogen bonds on the rate constants. The effect of π-complex formation on the reaction rate has also been observed for aromatic radicals such as diphenylnitric oxide.

As far as the present author is aware, the first ESR study of "live" chemically active radicals directly in the course of the reaction was carried out by Shlyapintokh and Tsepalov with the present author's participation, using as an example the liquid-phase chain oxidation of hydrocarbons[60]. The "classical" mechanism of such a process is as follows:

$$\text{decomposition of initiator} \xrightarrow{W_i} 2\,R_i^{\cdot} \rightarrow 2R^{\cdot},$$

$$\left.\begin{array}{l} \rightarrow R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \\ RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \end{array}\right| ,$$

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_3} \text{destruction}.$$

As long as the reaction proceeds, a steady-state concentration of RO_2 (the $R^{\cdot}$ radicals are more active and their number is much less) should be maintained:

$$[RO_2^{\cdot}]_{st.} = \sqrt{\frac{W_i}{2k_3}}.$$

The rate of oxidation is then

$$W = k_2[RH][RO_2^{\cdot}] = \frac{k_2}{\sqrt{2k_3}}\sqrt{W_i}\,[RH].$$

Since W and W_i are known, the combined rate constants $k_2/\sqrt{2k_3}$ have been determined for a long time for many reactions. The ESR method permitted the measurement of the steady-state concentration $[RO_2^{\cdot}]$, which led to the determination of both rate constants for the process.

The ESR signal due to $RO_2^{\cdot}$ peroxy-radicals, which consists of a singlet with a displaced g-factor $g = 2.015$, was first recorded in the oxidation of cumene. The reaction at 60–100°C was performed directly in the resonator, where a special device ensured a continuous supply of an excess of oxygen (otherwise the relation specified above would be invalid). Fig. 10 presents the results of the measurement of $[RO_2^{\cdot}]_{st}$ and their comparison with the available data for cumene, obtained by the method of discontinuous illumination. Good agreement between the results showed that ESR can be used to determine the rate constants k_2 and k_3 also as an independent method; the rate constants for the oxidation of diphenylmethane, diphenylethane, etc. were obtained in this way. Somewhat later the signal due to $RO_2^{\cdot}$ in the oxidation of cumene was investigated independently in a jet by Thomas[61], who showed that the radicals may be stabilised by the formation of a complex with pyridine.

Nowadays the study of active radicals in the liquid phase (with purely chemical initiation) is almost always carried out in flow systems. Such systems are now widely known and their design has been frequently described. The flow rates are usually 10–100 cm sec^{-1} and the idle time (from the instant of the mixing of the reactants to the instant when the resonator is reached) amounts to hundredths of a second. The advantage of flow systems is that it is possible to maintain a high reaction rate over a long period (i.e. a high rate of initiation of active centres) without having to worry about the consumption of the reactants: while under static conditions the time constant for the recording of a signal should be much less than the lifetime of a radical or the time required for the consumption of the reactants, in a jet apparatus the time required for the mixture to flow out is the only limiting factor. It can be shown that under optimum conditions the gain in sensitivity is approximately $\sqrt{V_0 V_c}$, where V_0 is the volume of liquid which has passed through the resonator during the time when the signal was recorded and V_c the effective volume of the capillary in the resonator. Depending on the experiment, this gain does in fact reach 10–20.

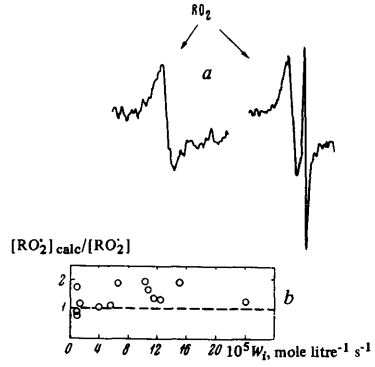


Figure 10. An example of the investigation of a liquid-phase reaction—chain oxidation of cumene[59]:
a) ESR spectra of cumenylperoxy-radicals; *b*) comparison of the calculated and experimental steady-state concentrations of radicals for different rates of initiation.

It has been shown in recent years that, it is possible with flow systems to obtain sufficient concentrations of active radicals at room temperature for recording ESR signals and for the investigation of the reactions of these radicals. In one of the first studies (using a jet) Dixon and Norman[62] obtained OH radicals by a reaction similar to Fenton's reaction:

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH^{\cdot} + OH^{-}.$$

By adding various alcohols to the system, it is possible to observe the transformation of the $OH^{\cdot}$ spectrum into the signal of the alcohol radical, which is evidence of a reaction of the type

$$O\dot{H} + CH_3OH \rightarrow H_2O + \dot{C}H_2OH,$$

Analysis of the secondary ESR spectra established that in saturated alcohols a hydrogen atom is always split off from an α-carbon atom, while in unsaturated compounds the incorporation of OH at the double-bond was observed.

Similar flow ESR studies on radicals obtained by a one-electron transfer reaction are now being carried out on a wide scale. These are described in greater detail in the review by Waters[63]. They are undertaken mainly in order to elucidate the structure of the radicals formed and hence the mode of the fundamental reactions, but evidently the technique also permits quantitative kinetic studies.

For example, Blyumenfel'd and coworkers[64] studied the kinetics of the reactions of OH^- ions (in a flow system) with tetracyanoethylene, p-benzoquinone, and o-naphthoquinone, which lead to the formation of the corresponding radical-ions. The activation energies were determined and the effect of ionic strength and the addition of oxygen, hydrogen peroxide, and certain anions was investigated. It was shown that the effect of hydrogen peroxide depends on the pH of the medium, since molecular and ionic (HO_2^-) forms of hydrogen peroxide exist at different pH.

Another possibility of the kinetic and structural study of active radicals in the liquid phase was demonstrated by Fessenden and Schuler[65] in the USA, who directly recorded the spectra of C_2H_5 radicals (concentration about 4×10^{13} cm^{-3}, dose rate 10^8 mrad h^{-1}) with specially adapted apparatus in the radiolysis of liquid ethane. So far they have investigated the ESR spectra of a number of active radicals ranging from CH_3, C_2H_5, and FO_2 to 2,2-diethyl-1-methylbutyl. It has been shown that in all cases the destruction of radicals is probably determined by their diffusion, since a change in the viscosity of the solution (by the addition of glycerol) alters significantly the steady-state concentration of the radicals.

The possibilities for the investigation of short-lived species have also been greatly extended by a method involving the accumulation of the useful signal[66]. The principle of this method consists in synchronised n-fold recording of the signal with subsequent summation, as a result of which the sensitivity increases by a factor $\sqrt{n}$. The accumulation method in effect permits longer recording times without risk of a drift in the zero line, etc.; as far as one can judge from published data, this results in a sensitivity gain by a factor of 10. In the study of short-lived species, this method can be very effective only in combination with a flow system whereby long recording times can be achieved. On the other hand, the accumulator can be synchronised with a source of active species, as was done by Piette[67] (USA). Simultaneously with the flash of the photo-source or a specified time afterwards the instrument was switched on and the signal was recorded (at one point): at each point corresponding to specified time intervals from the start of the flash, the signal was recorded 25 times. This yielded a kinetic curve for the destruction of the cumenyloxy-radical (obtained by the photolysis of cumenyl hydroperoxide) at room temperature, where the reaction time constant amounts to about 0.03–0.05 s. Piette[67] hoped to obtain in this way the rate constant for the removal of hydrogen from solvent molecules, but the identity of the constants in cumene, ethylbenzene, and toluene shows that even at 20°C the reaction rates are limited by diffusion. The method described would probably permit the investigation of rapid reactions in any phase ("active" radicals are investigated as "stable" radicals), but it should be noted that we are unaware of any other publications on this question after Piette's communication in 1963, apart from the data presented in Soutif's review[40] on the study of rapid ($\tau = 0.01$ s) oxidation–reduction reactions of enzymes with the aid of a low-inertia jet system produced by the Varian Company. The method is admittedly fairly complex experimentally and it is not always possible (only for $\tau > 0.1$ s) to record the entire ESR spectrum, so that correct kinetic data can be obtained only when the line form coefficient does not change.

The kinetics of rapid processes have been investigated not only on the basis of the intensity of the ESR signals, but also on the basis of changes in line form. If as a result of a fast exchange reaction there is a transition of the unpaired electron from one molecule to another, and the transition frequency ν is greater than the line width (in terms of frequency units), a broadening of the lines in the spectrum is observed and then (when $\nu > \gamma a$) also blurring of the hyperfine structure. This phenomenon was used as early as 1954 by Weissman[68] to study the electron exchange between paramagnetic molecules. However, the reaction rate must not be less than 10^7–10^8 s^{-1}. [The author probably means that the bimolecular rate constants lie in the range 10^7–10^9 l mole^{-1} s^{-1} (Ed. of Translation)]

The rates of electron exchange in paramagnetic complexes can be studied similarly. Exchange of this type in aqueous solutions of copper(II) complexes of ethylenediamine, ammonia, etc. has been studied in detail by Voevodskii and Zamaraev[61]. The observed effect is the broadening of all the components of the quadruplet signal of Cu^{2+} ions with decrease of the concentration of copper $(Cu)_0$ and then

$$\Delta H_i = \Delta H_i^{\circ} + \frac{k_1}{[Cu]_0} .$$

It has been shown[69] that in the region of line narrowing due to exchange the principal contribution to the variable component of line width ΔH_i^* comes from the isotropic hyperfine interaction, and

$$\gamma \Delta H_i^{\bullet} = \frac{5}{4} \frac{a_{Cu}^2}{\omega_l} .$$

Thus $\omega_i = k_i[Cu]_0$ and the exchange rate constant can be determined at room temperature:

$$k_i \simeq 10^9 \text{ litre mole}^{-1} \text{ s}^{-1}.$$

Finally, the broadening of the ESR line may also be used to investigate a rapid kinetic process such as collisions in a liquid[39]. At high concentrations of stable radicals line broadening δH_l is observed, associated with exchange relaxation during collisions, as suggested by Buchachenko. If p is the probability of such relaxation on collision, then the exchange frequency is

$$\nu_i = \gamma \delta H_i = p k_2 \frac{Z n_r}{n_s} ,$$

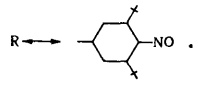
where k_2 is the number of collisions per unit time, n_r and n_s are the concentrations of the dissolved radicals and solvent molecules, and Z is the coordination number of the cage.

Assuming that $p \simeq 1$ and measuring the broadening δH_i at various n_r, it is thus possible to determine k_2 and, by making measurements at various temperatures, also the activation energy for the collisions. For 2,4,6-tri-t-butylphenoxyl in benzene and ethylbenzene, we have

$$k_2 = 3.5 \times 10^{-10} \exp\left(\frac{-2200}{RT}\right) \text{ cm}^3 \text{ s}^{-1}.$$

Recently Buchachenko and coworkers initiated on the investigation of collisions between the ends of the same molecules by studying line form changes in the ESR spectra

of biradicals and polyradicals[70]. They managed[70] to investigate the ESR spectra of nitrogen oxide radicals of the form R'–R, $ROOC(CH_2)_4COOR$, and others, where



It was found that the hyperfine structure corresponds to splitting by all the nitrogen atoms. Since in this case there is no possibility of electron delocalisation, it was suggested that electron exchange takes place as a result of the collisions between the paramagnetic ends of the molecule on the "claw" principle. In fact the frequency of the "averaging out" of the hyperfine structure proved to depend on the temperature and the structure of the central bridge. On the basis of a model involving special modulation of isotropic hyperfine interaction, developed by Freed and Fraenkel[44], it is possible to calculate further the frequency of the exchange interaction by the formula

$$\Delta H_i(\pm 1) - \Delta H_i(\pm 2) = \frac{1}{8}\gamma a_N^2/\nu_i ,$$

where $\Delta H_i(\pm 1)$ is the line width for the components with $\Delta m_N = \pm 1$ and ± 2 and a_N is the constant for the hyperfine splitting by nitrogen. It has been found that, for biradicals with pronounced exchange, ν_i is in the range 10^7–10^8 s^{-1}, with $\nu_i^0 \simeq 10^8$–10^9 s^{-1} and $E_i \simeq 1$–3.5 kcal mole^{-1}.

Thus application of electron spin resonance in the study of reactions in gas and liquid phases has been developing in the following ways.

1. The study of the mechanism of complex reaction by analysing (on the basis of the ESR spectra) the structure of the radicals formed in the process.
2. The determination of the rate constants for various radical reactions from the changes in the intensity of the ESR signals. Here the ESR method is used as a very sensitive and selective analytical procedure.
3. The determination of the mechanism and kinetic constants of fundamental reactions from the steady-state concentrations of the paramagnetic centres generated by the chemical reaction or external radiation (for a known rate of initiation).
4. Quantitative study of fast chemical and physicochemical processes (exchange reactions, collisions) on the basis of the changes in the width and form of ESR lines as a result of the paramagnetic relaxation induced by these processes.

3. Reactions in Solids

The study of chemical processes in the solid phase by the ESR method must be considered in greater detail, since in this field electron spin resonance is at present the most universal method for the investigation of fundamental reactions. The application of the ESR method led to the discovery of a very interesting field of radical chemistry, previously experimentally inaccessible, the study of radical reactions initiated by light, hard radiation, and chemical reactions in solids.

Examination of the specific questions associated with the application of electron spin resonance in photochemistry and radiation chemistry (the so called high-energy chemistry) is outside the scope of the present review. Here only the most interesting advances in this field will be briefly described (see Voevodskii's review[71]). By the stabilisation of radicals at low temperatures, the primary radicals formed on irradiation proved to be so stable that their chemical structure can be determined by the ESR method and sometimes it is possible to obtain information about their geometrical structure and orientation in the matrix. The study of the chemical nature of radiation damage at the instant when only a fraction of 10^{-8}–10^{-10} of all the molecules have been damaged leads of course to a completely new approach to the elucidation of the mechanism of this effect. ism of this effect.

A significant advance in these investigations was made in the Soviet Union in 1958–1960 when the formation of radicals during irradiation by ultraviolet light and fast electrons was investigated. Subsequent studies permitted a clear separation of the primary and secondary processes much more reliably than before, the determination of the radiation yields of chemical damage (i.e. the number of bond dissociations per 100 eV of energy absorbed), and the finding that the dominant chemical step in the radiolysis of hydrocarbons is the dissociation of C–H bonds. The same measurements led to unambiguous demonstration of energy migration preceding the primary dissociation and the formulation of the general hypothesis concerning the dependence of the radiation stability of hydrocarbons on structure (see, for example, Refs. 72 and 73). The structure of the ESR spectra showed that the breakdown of chemical compounds takes place with formation of the same radicals almost independently of the type of influence on the system —ranging from ionising irradiation and photo-irradiation to high-frequency discharge[74] and mechanical degradation[75]. It has also been shown that these influences can themselves initiate further reactions of the radicals produced[76–78].

In the field of purely photochemical investigations, the determination of the mechanism of a number of sensitised photochemical reactions[79], the observation and study of signals from triplet molecular states[80], and the study of two-quantum reactions[81] may be mentioned as interesting advances achieved with the aid of electron spin resonance. However, the application of electron spin resonance in the investigation of "stabilised" radicals is by no means confined to primary reaction steps. By studying the change in the ESR spectrum on heating the specimen, under the influence of various additives, and on repeated irradiation of the system with light of different wavelengths, etc., it is possible to obtain exceptionally interesting (both for radiation chemistry and for chemical kinetics in general) data on the mode and rates of the fundamental reactions in the solid phase, approximately in terms of the scheme formulated above for liquid-phase reactions. One of the most effective examples of reaction mechanism elucidation is the unambiguous demonstration of the existence of the so-called "adhesion" radical formed by a reaction of the type $H^{\cdot} + C_6H_6 \rightarrow C_6H_7^{\cdot}$.

The ESR spectrum of C_6H_7 radicals should of course differ sharply in its hyperfine structure (three lines with $a \simeq 46$ Oe × a quartet with $a \simeq 10$ Oe) from the spectrum obtained in the usual reaction of phenyl radicals C_6H_5 (four lines with $a = 18$ Oe × three lines each with $a = 8$ Oe).

C_6H_7 radicals were identified in solid benzene in 1961 (almost simultaneously) by Buben and coworkers[82], Fischer[83], and somewhat later by two groups of investigators in the USA[84,85]. Then it was shown, by direct experiments on the interaction between atomic hydrogen and benzene in the gas phase and the same reaction in the solid phase in a specially prepared solid matrix containing, at the beginning of the experiment, H atoms stabilised at 77 °K and molecules of aromatic compounds, that atomic hydrogen does indeed adhere to aromatic molecules. Analysis of the hyperfine structure of the ESR spectra of the radicals formed in the interaction of hydrogen atoms with various phenols actually permitted the determination of the site of adhesion of the H atom in each individual case[86].

One of the first quantitative studies on the kinetics of radical reactions was undertaken by Voevodskii et al.[85], who determined the rate constants for the reactions $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$, $RO_2^{\cdot} \rightarrow R^{\cdot} + O_2$, etc. involving fluoroalkyl radicals in irradiated polytetrafluoroethylene and also measured the diffusion coefficients of O_2, H_2, and NO in Teflon and the radical recombination rate constants. Measurements were made at the same time of the heat of the reversible oxygen elimination reaction: $\Delta H_{R-O_2} = -6$ kcal mole^{-1}. Quite recently Janzen et al.[88] reported the measurement of the heats of the reaction of triphenylmethyl radicals with oxygen $\Delta H_{R-O_2} = -9$ kcal mole^{-1}. The radicals were obtained by γ-irradiation of triphenylacetic acid.

In principle, when the above methods are used for the measurement of concentration, the determination of kinetic curves (the time variation of the intensity of the signal) and their treatment by the usual methods of formal kinetics do not present special difficulties; for a unimolecular reaction, $\ln([R^{\cdot}]/[R^{\cdot}]_0) = -k_1 t$, for a bimolecular reaction, $1/[R] - 1/[R]_0 = k_2 t$, etc. However, further interpretation of these data does present a fundamental difficulty. The point is that when we measure by the ESR method say, the rate of disappearance of $R^{\cdot}$ radicals by the reaction $R^{\cdot} + R^{\cdot} \rightarrow M$ in a condensed phase, then the measured rate constant is not in general a fundamental constant. If we denote by k_m an average frequency of migration of the radical from one cage to another (diffusion coefficient $D = \frac{1}{6}\lambda^2 k_m$), then the number of collisions of radicals in a single cage with a volume V^* is $k_m V^*$. However, in the simplest case the probability of reaction is then $k_i/(k_i + k_m)$, where k_i is the rate constant for the intrinsic chemical reaction $|R^{\cdot} \ldots R^{\cdot}| \rightarrow M$ in the cage. Thus one measures the effective constant

$$k_2 = \frac{k_i k_m V^*}{k_i + k_m} . \qquad (4)$$

Consequently, for fast reaction where $k_i \gg k_m$, one measures essentially the rate constants for diffusion, $k_m V^* \sim D\lambda$, and only for slow reactions, where $k_i \ll k_m$, is it possible to measure the rate of the reaction itself. These considerations must be taken into account when electron spin resonance is used to study kinetic processes in solid and liquid phases. For reactions of stabilised radicals with mobile molecules, usually $k_m \gg k_i$, but when only stabilised radicals participate in the reaction, measurements are as a rule made on "diffusion" kinetics[89,90]. The cage effect can be taken into account similarly also in unimolecular decomposition reactions in the condensed phase; if k_i is the true rate constant for decomposition and k_t the rate constant for the reverse reaction in the cage, then the probability of emergence from the cage is $f = k_m/(k_m + k_t)$, and the measured rate constant for decomposition is

$$k_1 = \frac{k_i k_m}{k_m + k_t} = f k_i . \qquad (5)$$

With these simple hypotheses at our disposal, we shall examine in greater detail several examples of the application of electron spin resonance in the study of fundamental reactions in the solid phase.

a. Recombination Kinetics and Spatial Distribution of Paramagnetic Centres in the Solid Phase

When specimens containing free radicals accumulated in them at a low temperature (usually 77°K) are heated, the concentration of the radicals begins to decrease at certain temperatures and the kinetics of the recombination reaction can be studied from the decrease of the intensity of the ESR signal. It follows from the above considerations that it is then possible to measure the constants k_m, i.e. to obtain information about the mobility of free radicals.

Thus Buben and coworkers[91] measured the rate of recombination of radicals in irradiated cyclohexane near the gas-crystalline transition temperature state; the reaction kinetics were described by a second-order equation:

$$-\frac{dn}{dt} = k_2 n^2 \qquad (6)$$

and the measured radical mobility constant k_m agreed satisfactorily with the self-diffusion coefficients already available from NMR data. Similar measurements were made for a number of more complex organic substances and polymers at temperatures close to the melting point or a phase-transition temperature[87,89,92]; these measurements led to the hypothesis that in most cases the mobility of active centres is not determined by the diffusion of the molecules in the usual sense but by the transfer of the active centre by reactions of the type

$$R^{\cdot} + RH \rightarrow RH + R^{\cdot},$$
$$M^{-} + M \rightarrow M + M^{-} \quad \text{etc.}$$

However, in a very large number of cases the destruction of paramagnetic centres does not obey simple relations of the type of Eqn. (5). Two types of deviation are observed.

1. After heating at high initial radical concentrations, there is initially a sharp fall of the intensity of the ESR spectrum by a certain amount and then "steady-state" destruction begins described by Eqn. (6).[93]

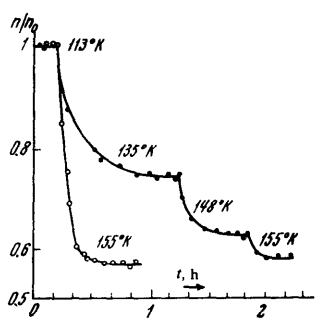


Figure 11. Stepwise kinetics of the recombination of free radicals in β-irradiated phenol[94].

2. The destruction of radicals at temperatures far removed from the melting point or a second-order phase transition is in most cases "stepwise", i.e. at each temperature a definite concentration of paramagnetic centres remains[94]. The experimental curves illustrating these phenomena are presented in Figs. 11 and 12. The behaviour of the destruction curves over a wide range of initial concentrations n_0 is independent of the latter, i.e. the curves can be made to coincide after replotting in terms of the coordinates n/n_0 and t. Nevertheless, the rate of normal recombination [Eqn. (6)] should depend significantly on n_0.

Both these kinetic phenomena can be explained if it is assumed that the paramagnetic centres are not distributed uniformly throughout the solid substance but in groups or

pairs[93,94]. Consequently the concentration of paramagnetic centres determined from the ESR signals does not reflect their true density in the specimen. Thus, we return to the problem formulated in Section II (Subsection 2)—the problem of the measurement of local concentrations of paramagnetic species. Attempts at such estimates were made on the basis of the measurement of the dipole–dipole contribution to the ESR line width either directly[10] or by the method of successive saturation[14,17,18] and the electron spin-echo method[13]. In general, these measurements confirmed (so far semiquantitatively) the conclusion concerning the possibility of non-uniform distribution of radicals in irradiated solids. Similar non-uniform distribution of paramagnetic centres has been detected in frozen solutions of stable radicals (diphenylpicrylhydrazyl[95]) and in a non-radical system[96] (frozen solutions of the ions Mn^{2+} and Gd^{2+}), where the non-uniformity is due to segregation. The study of this effect is also very important chemically.

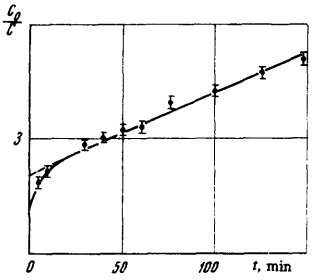


Figure 12. Kinetics of the recombination of free radicals in γ-irradiated polyethylene (according to the data of A.Arvia et al., see Lebedev[93]) [This is probably a reference to A.J.Arvia, F.Cracco, and M.Dole, J.Chem.Phys., 37, 2449)1962) (Ed. of Translation).]

At the present time new data have been obtained by the ESR method, concerning the non-uniform distribution of "heavy" radiation defects and also of dissolved paramagnetic centres in crystallising systems.

b. H–D Exchange Reactions of Free Radicals in Irradiated Amino-Acid Single Crystals.

Isotope exchange is one of the direct methods for the investigation of mechanism and reactivity and therefore the present author attaches great interest to the data published recently concerning the solid-phase H–D exchange in free radicals stabilised in irradiated single crystals of amino-acids—alanine[97], aspartic acid[98], and (indirect data) glycine[99]. The authors of these investigations made no attempt to explain in detail the chemical mechanism of the reactions, but it was shown that the ESR method reveals the successive substitution of H atoms in the aliphatic chain in partially deuteriated (at the sites containing mobile protons) amino-acids, and a detailed investigation of the kinetics of the changes in the ESR spectra made gave the kinetic constant for the reactions of aspartic acid. Together with Almanov, the present author made a similar study[100] of possible H–D exchange in the previously uninvestigated single crystals of DL-serine (monoclinic system, symmetry class C_{2h}, monoclinic angle 106°) grown from a solution in 90% D_2O:

$$DO{-}CH_2{-}CH(ND_3^+){-}CO_2^-.$$

After irradiation at room temperature from a cobalt-60 γ-source with a dose of about 20 mrad, the ESR spectrum was as in Fig. 13*a*, which corresponds (see Section II, Subsection 4) to radicals of the type

$$DO{-}CH_2{-}\dot{C}H{-}COOD.$$

In the orientation corresponding to $H_0 \parallel b$, $\Delta H_\alpha = 23$ Oe, $\Delta H_\beta = 40$ Oe, and $\Delta H_{\beta'} = 14$ Oe. On further heating of the single crystal to 50–100°C, the ESR spectra changed significantly, as shown in Fig. 13*c*, the total concentration of radicals not decreasing by more than 20%. Analysis of the structure of the ESR spectra presented in Fig. 13 indicates the occurrence of the following consecutive reactions:

$$-CH_2{-}CH_2 \xrightarrow{(1)} CHD{-}CH{-} \xrightarrow{(2)} -CDH{-}CD{-} \xrightarrow{(3)} -CD_2{-}CD-.$$

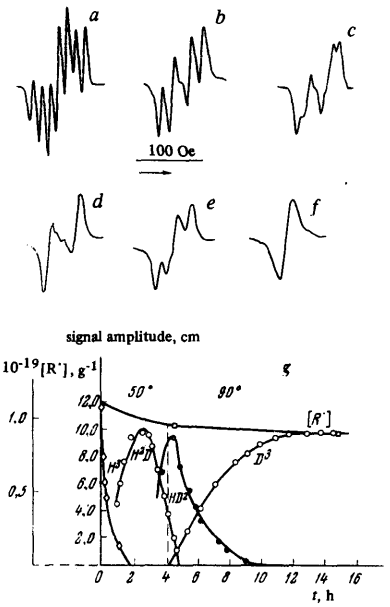


Figure 13. An example of the investigation of H–D exchange in the solid phase—exchange undergone by free radicals in γ-irradiated DL-serine[98]:
a) ESR spectrum obtained after γ-irradiation of a deuteriated single crystal at room temperature; *b*)–*f*) changes in the spectrum as a result of successive heat treatment for 2 h at 50°C (*b*), 4 h at 50°C (*c*), 2 h at 90°C (*d*), 4 h at 90°C (*e*), and 10 h at 90°C (*f*); *g*) kinetics of the change in the overall concentration of R· and the concentration of radicals corresponding to different degrees of substitution of α- and β-protons by deuterium.

Fig. 13*g* shows the kinetic curves determined from the intensities of the corresponding components of the hyperfine structure, which also indicate the occurrence of the irreversible consecutive reactions $H^3 \rightarrow H^2D \rightarrow HD^2 \rightarrow D^3$. The variation of the reaction rate with temperature corresponds to $E_1 \simeq 25$ kcal mole^{-1} and $k_1^0 \simeq 5 \times 10^{13}$ s^{-1} for reactions (2) and (3); according to previous data, E does not differ appreciably from E_1, but k^0 is significantly smaller than k_1^0. The findings described here are thus

almost completely consistent with the results obtained earlier for alanine and aspartic acid[97,98].

On the basis of the available data[97-100], the following interesting features of H–D exchange reactions in the solid phase may be noted.

1. The reaction involves free radicals only.
2. The reaction is stereospecific, i.e. the protons located in different positions relative to the free valence are substituted in a definite sequence. Of the two β-protons, the one whose hyperfine splitting constant is smaller is substituted first.
3. In irradiated methylsuccinic acid the reaction virtually does not take place, although the radical formed is quite similar (H^3).
4. The reactions are irreversible up to the complete substitution of all the hydrogen atoms in the radical.

The last finding immediately excludes the hypothesis that the exchange takes place within the limits of a single molecule or crystal unit cell: since $\Delta G \simeq 0$, equilibrium should then be established between the deuteriated and the initial radicals. It must be postulated that the exchange reaction is of second order and the concentration of H donors is much higher than the concentration of radicals, i.e. there is a possibility of the transfer of deuterium and hydrogen atoms over long distances, a possibility which has been frequently postulated to account for the kinetics of radical reactions in solids[74,90]. The present author believes that in the present concrete case the transfer of deuterium atoms can be achieved via molecules of D_2O of crystallisation, which are known[101] to be entrained in crystalline amino-acids in an amount approximately equal to the number of molecules of the acid and which probably acquire diffusional mobility at 50–100°C. Then the exchange mechanism can be represented thus:

$$-CH_2-\dot{C}H- + D_2O \rightarrow -CH_2-\underset{\displaystyle D}{\overset{\displaystyle O}{\overset{/\quad\backslash}{C}}}-CH- \rightarrow -\dot{C}H-CHD + HDO,$$

$$-\dot{C}H-CHD- + D_2O \rightarrow -CHD-\dot{C}D- + HDO,$$

$$-CHD-\dot{C}D- + D_2O \rightarrow -CD_2-\dot{C}D- + HDO.$$

The suggested reaction mechanism explains in broad outline the experimental findings 1–4, but is of course only a preliminary hypothesis. In principle, the role of D_2O can be fulfilled by D_2 or ND_3 (however, $[D_2]$, and $[ND_3] \simeq [R^\cdot]$, while $[D_2O] \gg [R^\cdot]$). On the other hand, the general conclusion concerning the possibility of a solid-phase bimolecular exchange reaction in which the rate-limiting stage is the transfer of hydrogen seems to be adequately justified. Further study of the kinetics of such reactions can provide valuable information about fundamental processes in the solid phase.

c. Kinetics of the Polymerisation of the Oligomers of Acrylate Esters

The description of the application of electron spin resonance in the study of polymerisation reactions might have constituted a large section of the present review‡. One may refer to studies on growing-chain radicals[102,103], the cross-linking of polymers under the action of radiation[104], etc. However, here this problem is examined only as part of the general problem of solid-phase reactions, using a single concrete example.

‡ See, for example, the review of Buchachenko et al. on electron spin resonance in polymers[114].

Korolev et al.[105] made a series of studies by the ESR method on the initiation of polymerisation and polymerisation kinetics at advanced stages. They investigated the ESR signals from radicals entrained in the course of thermo- or photo-initiation of the three-dimensional polymerisation of acrylate ester oligomers—such as butylene glycol dimethylacrylate and others. They used phenyl peroxide, azobisisobutyronitrile, etc. as initiators. The typical radical accumulation curve in thermally initiated polymerisation has a maximum, according to Smirnov et al.[105] The decrease of the intensity of the ESR signal after prolonged periods is evidently associated with the disappearance of the initiator. In accordance with Eqn. (5) derived above, the rate of decomposition is

$$W_i = fk_i[I]_0 e^{-k_i t},$$

where f is the efficiency of the initiation and $[I] = [I]_0 e^{-k_i t}$ is the initiator concentration. The equation describing the accumulation of radicals is

$$\frac{d[R^\cdot]}{dt} = W_i - k_2[R^\cdot]^2,$$

whence

$$[R^\cdot] = \sqrt{\frac{W_i}{k_2}}\tanh\sqrt{W_i k_2}t),$$

at small values of t, i.e. at the beginning of the curve we have

$$[R^\cdot] \simeq W_i t = fk_i[I_0].$$

For large values of t, one may assume that $\tanh(\sqrt{W_i k_2}t \simeq 1$: then $\ln[R^\cdot] = \text{const.} - \frac{1}{2}k_i t$.

Hence it is clear that one can estimate from the experimental curve a quantity which is very important chemically —the initiation efficiency. Admittedly, it is assumed that the radicals which did not emerge from the cage give rise to the same initiator I molecule. The photo-initiation kinetics can be investigated similarly. In particular, Smirnov et al.[105] concluded that polymerisation in the systems investigated is initiated by a radical-acceptor mechanism of the type

$$R_i^\cdot + \underset{|}{\overset{|}{CH_2}} \rightarrow R_iH + \underset{|}{\overset{|}{\dot{C}H}}.$$

This conclusion is confirmed by the ESR spectra of radicals (doublet with a splitting of 22.5 Oe) recorded at −10°C. On raising the temperature to 80°C, it is converted into a signal of the growing-chain radical, which is subsequently in fact entrained in the polymer.

d. Detection of Radical Pairs and the Study of the Cage Effect

The characteristics of chemical reactions in condensed phases can be associated to a large extent with the Franck–Rabinowitch cage effect, which so far has been inferred solely from kinetic data, since there exists no direct method for the detection of species in the "cage". Nevertheless, in principle the ESR method makes it possible to distinguish the free radicals in the "cage" from isolated radicals, since the mutual approach of paramagnetic centres to a distance up to 5–10 Å should entail the appearance in the ESR spectrum of dipole–dipole and exchange interaction of electron spins. Recently data have been published on ESR spectra of radical pairs stable at the temperature of the measurement for large concentrations of radicals entrained in single crystals[106,107] and glasses[108].

The radical pairs formed in the cage during a real chemical process cannot of course be stable, but, if their steady-state concentration is not too low, it is evident from what has been said above that in principle they might be detected by the ESR method. Recently the present author succeeded in showing[109] that "active" radical pairs can indeed be detected directly during the low-temperature photochemical decomposition of azobisisobutyronitrile (AIBN) and in measuring the probability of the emergence of the radicals from the "cage" by the ESR method. AIBN is known to decompose readily into two radicals with evolution of a nitrogen molecule; by virtue of the high rate of initiation of the pairs and the relatively large distance between the radicals in the cage, relatively high concentrations of pairs can be obtained in this case. Earlier the present author observed together with Shuvalov and Zhuravleva[110] that, apart from the ESR spectrum due to the radicals $(CH_3)_2C(CN)$, which consists of a septet (a_H = 21 Oe) of triplets (a_N = 7 Oe) (see the analysis of this spectrum in Fig. 14), a signal unusual for this system, namely a doublet with a splitting of about 160 Oe and an additional hyperfine structure, appears in the first minutes of the photolysis of AIBN. Next the author postulated that this signal is due to radicals which failed to emerge from the cage, and carried out spectroscopic and kinetic studies which confirmed this hypothesis.

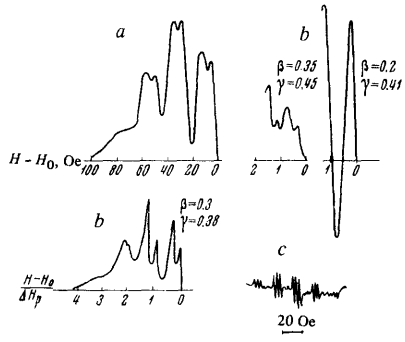


Figure 14. Analysis of the ESR spectrum of the cyanoisopropyl radical based on the comparison with calculated line form: *a*) ESR spectrum of the radicals produced in the photolysis of azobisisobutyronitrile; *b*) calculated spectra corresponding to different ratios $\beta = \Delta H_n/a_N$ and $\gamma = a_N/a_H$; *c*) spectrum obtained in the thermal decomposition of azobisisobutyronitrile in the liquid phase[110].

AIBN specimens obtained in the form of a crystalline powder were photolysed with light from a DRSh lamp in the resonator of an EPR-2 spectrometer of the Institute of Chemical Physics at 77°K; to prevent heating by the light, the tube with the specimen was filled with liquid nitrogen. When the light was switched on (effective spectrum with $\lambda < 330$ nm), the signal I shown in Fig. 15*a* appeared—a doublet with a splitting of 160 Oe and an additional hyperfine structure consisting of 11 lines with intensity ratios of approximately 1 : 5 : 20 : 45 : 75 : 90 : 75... In the course of further photolysis this spectrum is accompanied by the appearance of another (Fig. 15*b*), which is stable at 77°K, while the doublet signal disappears 30 s after the light is switched off (Fig. 15*c*). When the experiments were performed with isolated crystals, there appeared in spectrum I yet another similar system of lines II, the doublet splitting in which changed from 0 to 300 Oe on rotating the crystal. Spectra I and II can be attributed to the radical pair (R'...R'), since here one should in fact observe spin-spin splitting, changing on rotation of the single crystal from $D_\perp = D_0$ to $D_\parallel = -2D_0$ according to the law $D = D_0(1-3\cos^2\theta)$. The orientation-independent signal in the single crystal can be due to an admixture of an amorphous phase or other causes, which are not discussed here, since we did not have at our disposal "true" single crystals with indexed crystallographic axes. Therefore the principal conclusions were based on the study of the signals I in polyoriented specimens.

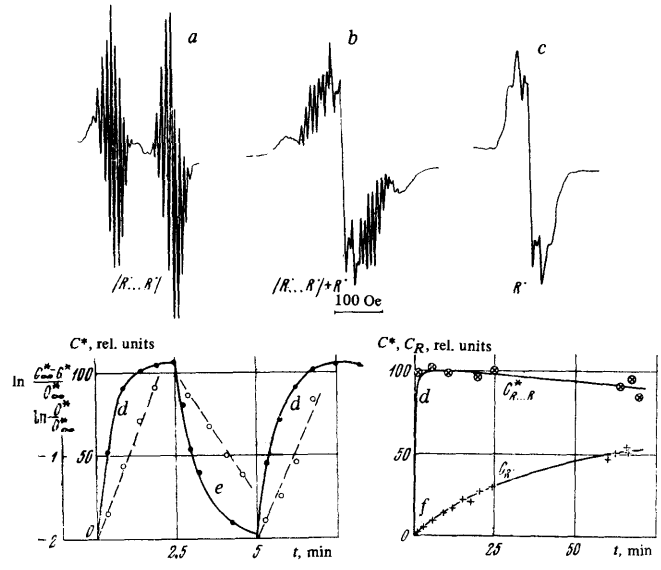


Figure 15. ESR spectra (*a*, *b*) and the kinetics of the formation (*d*) and destruction (*e*) of radical pairs and radicals [*c*) spectrum; *f*0 accumulation kinetics] in the photolytic breakdown of azobisisobutyronitrile[109].

At first sight the possibility of the observation of a strongly anisotropic signal in polycrystalline specimens appear strange. However, the point is that in the case of axial splitting anisotropy, which obtains here, the probability of perpendicular orientations is greatly enhanced and the spectrum shows almost only the lines corresponding to this orientation. Fig. 16*b* shows a calculated ESR spectrum made up of "asymmetric" lines (without taking into account the additional hyperfine structure)[25]. This spectrum agrees satisfactorily with the experimentally observed spectrum of AIBN powder when the latter is recorded over a wide range of scan of the magnetic field and the hyperfine structure is artificially "blurred" (Fig. 16*a*). Analysis of the experimental spectra showed that the splitting of 160 Oe observed in experiments with AIBN powder corresponds to $D_\perp$, which in turn corresponds to dipole–dipole interaction between electron spins over a distance of 5.6 Å, approximately the same as the distance between the radicals in the initial molecule. Finally, the additional hyperfine structure can be due to splitting by the 12 protons present in the pair (only 11 lines are shown, since the two

extreme components have an intensity lower by a factor of 10; the calculated intensity ratios of the observed 11 components, 12 : 66 : 220 : 495 : 792 : 924 : 792:..., are in agreement with experiment). It is interesting that the splitting by the protons is smaller by a factor of 2 than in isolated radicals and that all the protons are equivalent, in agreement with the theoretical postulate of Kurita and Kashiwagi[107], according to which the structure of the spectrum of the radical pair is described by the relation (taking into account the fact that $a_N \ll a_H$):

$$H = \frac{h\nu}{g\beta} \pm \frac{D}{2} - \frac{1}{2}\sum a_H m_H .$$

In contrast to the work of Kurita and Kashiwagi[107], who investigated stable radical pairs in dimethylglyoxime, the present author failed to observe signals corresponding to $\Delta M_S = 2$, which is probably due to an insufficient concentration of the pairs and the fact that the intensity of the signal with $\Delta M_S = 2$ is smaller approximately by three powers of 10 than the intensity of the main spectrum.

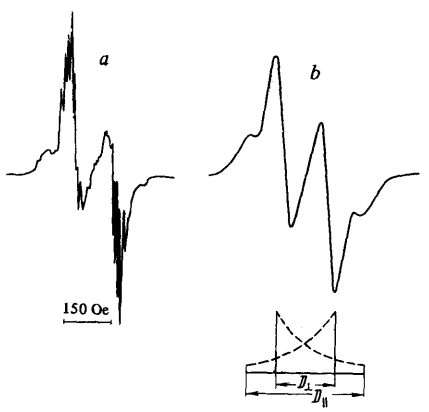


Figure 16. Experimental and calculated (without hyperfine structure) line form of the ESR signal due to polyoriented radical pairs.

It is also interesting to note that in their experiments on the low-temperature photolysis of AIBN, Ayscough et al.[111] obtained an ESR spectrum which they interpreted as a quintet with a splitting of 60–70 Oe and attributed to the radical R–N=N·. The present author regards this interpretation as insufficiently unambiguous, since the spectrum recorded with the signal only slightly greater than the noise can constitute the sum of the spectra of the "pair" |R·...R·| and isolated cyanoisopropyl radicals (see Fig. 15*c*).

Fig. 15 presents the result of an investigation of the kinetics of the accumulation and destruction of "pairs" and also the accumulation of radicals; these results are consistent with the above hypotheses. The transformed curves in Fig. 16*e*–16*f* show that the accumulation of "pairs" on illumination and their disappearance in the dark are consistent with destruction by a first-order reaction with approximately the same rate constant $k_1 = 0.03 \pm 0.01$ s^{-1}. On the basis of the usual kinetic mechanism of "cage" decomposition [Eqn. (5)], it is not difficult to show that the ratio of the initial yields of individuals radicals and radical pairs is equal to the probability of the emergence of the radicals from the cage. Nor can one exclude the possibility that the photochemical decomposition of AIBN takes place by the mechanism

$$M \rightsquigarrow |R\cdot\cdots R\cdot|^* \rightarrow R\cdot + R\cdot$$
"hot" pair
$$\downarrow$$
$$M' \leftarrow |R\cdot\cdots R\cdot|$$
thermolysed pair

which differs somewhat from the "classical" mechanism, but such a change in mechanism does not affect the determination of f. From the data in Figs. 15*d*–15*f*, one can estimate that $f = (1\text{–}3) \times 10^{-2}$, which is in satisfactory agreement with the value of f obtained by Smirnov et al.[105] for the decomposition of AIBN in polymeric matrices (admittedly for very much higher temperatures).

The following equation has been obtained for the rate constant for the destruction of cyanoisopropyl radicals in the AIBN cage in the temperature range 63–77°K:[112]

$$k \simeq 10^8 \exp(-3500/RT)\ (s^{-1}).$$

Thus with AIBN as an example, it proved possible to investigate directly the cage effect by the ESR method§. The possibility of direct determination of the probability of emergence from the cage and the constants for the decomposition and entrainment of radical pairs can prove extremely useful for the elucidation of the detailed mechanism of the cage effect. To an equal extent, it is interesting to investigate the structure of the spectra of radical pairs, the electronic structure of which has much in common with the electronic structures of both molecules in the triplet state and activated complexes in recombination–dissociation reactions.

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The scope of the application of electron spin resonance in the study of the kinetics and mechanism of chemical processes has been examined. A fairly wide range of problems has been covered, but certain specific questions, such as the study of catalysis and reactions on the surface, electrochemical reactions, biological processes, etc. have not been touched upon at all. It should be understood that the separation of problems associated with the study of the kinetics and mechanism of reactions from structural and chemical investigations is purely arbitrary. Frequently such investigations are carried out simultaneously. In particular, one of the most interesting problems of chemical physics involves the comparison of data on the structure and kinetics (reactivity) of free radicals. Electron spin resonance is a very suitable method for this purpose, because for example, it makes it possible to measure the spin density of the unpaired electron ρ_S at different centres (the spin density is in some measure usually related to electron density) and to determine simultaneously the rate constants for the reactions of the atoms split off. In principle, one may hope to observe a correlation between these two quantities, which would permit the prediction of chemical activity on the basis of hyperfine structure data. However, sufficient quantitative data are not as yet available for a test of such a correlation. Thus in the studies on H–D exchange[97–100] described towards the end of Section III the hyperfine structure constants and H–D exchange rate constants for all the protons (α, β, and β') of the aliphatic chain were determined for three substances. However, the difference in the rates is due to the differences

§ At the present time radical pairs have been investigated also in the decomposition of tetraphenylhydrazine and certain organic peroxides[115].

between the pre-exponential factors and is probably associated with geometrical factors. The activation energies E (the correlation of which with ρ_S appears most likely) are indistinguishable because of the considerable error in the determination. Admittedly, more promising results have also been published recently. For example, Solodovnikov et al.[113] investigated by the ESR method the distribution of spin density in 4-aryl-2,6-di-t-butylphenoxy-radicals simultaneously with the investigation of the reactivity of these radicals in reactions with peroxides and oxygen. The measured activation energies range from 9.9 to 11.9 kcal mole^{-1}, the accuracy being 0.2 kcal mole^{-1}. Carbon-13 has been used to measure the spin density at a reaction centre—the tertiary carbon atom of the C_6H_5–C_6H_5 bond. A fairly clear correlation between ρ_S and E was obtained in this investigation.

Even the artificially restricted range of problems which could be discussed here appears to show quite convincingly that the ESR method has already found wide application in chemical studies but that its possibilities are by no means completely discovered. Further development of the application of electron spin resonance in chemistry will probably involve both thorough and comprehensive use of the information contained in the ESR spectra and a rational combination of the ESR method and other physical and chemical techniques.

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Oxidation of Sterically Hindered Phenols

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The homolytic oxidation of sterically hindered phenols has been reviewed. The possible criteria of the reactivity of phenolic compounds, the properties of phenoxy-radicals–the primary products of oxidation by bound oxygen in non-polar media, and the kinetics of the reactions of phenoxy-radicals in the presence and absence of oxidants, have been discussed. Particular attention has been devoted to the oxidation of sterically hindered phenols in polar media by molecular oxygen, which exhibits a number of characteristic features. The bibliography comprises 84 references.

CONTENTS

I.	Introduction	421
II.	Criteria of the reactivity of phenolic compounds	421
III.	Properties of phenoxy-radicals—primary phenol oxidation products	424
IV.	Fundamental reactions of phenoxy-radicals: recombination, isomerisation, disproportionation, and reaction with oxygen	425
V.	Oxidation of sterically hindered phenols by molecular oxygen in polar media	430

I. INTRODUCTION

In recent years there has been an exceptionally vigorous development of the chemistry of sterically hindered phenols. To a high degree, this is due to practical requirements, the phenols being used to suppress undesirable free-radical (chain) processes. Various sterically hindered phenols are widely employed as effective antioxidants for the stabilisation of polymers, for the inhibition of the oxidation processes of fats used as food, etc.[1,2]

Considerable interest attaches to the chemistry of phenols from the standpoint of their role in biochemical processes[3]. In this connection the study of the mechanism of the oxidation processes of sterically hindered phenols assumes special importance. The present review deals with the homolytic oxidation of sterically hindered phenols. Reactions of type (1) and (2) take place under the influence of homolytic oxidants:

$$R_2R'H_2C_6O{-}H \rightarrow R_2R'H_2C_6O\cdot + \cdot H\ , \qquad (1)$$

$$(R_2R'H_2C_6O{:})^- \rightarrow R_2R'H_2C_6O\cdot + e\ . \qquad (2)$$

Processes of the first type include reactions of phenols with peroxy-radicals[4,5], diphenylpicrylhydrazyl (DPPH)[6,8], and tri-t-butylphenoxy-radicals[9,10]. One-electron processes of type (2) take place under the action of oxidants such as potassium hexacyanoferrate(VI)[11-14], potassium permanganate[15], cerium sulphate[16], and molecular oxygen in alkaline media[16,17]. The products of reactions (1) and (2) are phenoxy-radicals. Most of the work on the oxidation of sterically hindered phenols has been devoted to the identification of the phenoxy-radicals, the study of their properties, the reactions with oxidants, and the identification of the final oxidation products. On the other hand, the studies on the kinetic features of the behaviour of phenoxy-radicals are relatively few. In the examination of the available data on the oxidation of sterically hindered phenols particular attention will be given to the kinetics and mechanism of oxidation.

II. CRITERIA OF THE REACTIVITY OF PHENOLIC COMPOUNDS

The ease of the homolytic dissociation of the O–H bond in phenol is due to the dissociation energy of this bond. Accurate values of bond dissociation energies have been

determined mainly for simple organic molecules[18]. Accurate bond energies have been obtained only quite recently for several sterically hindered phenols[19]. To a first approximation, the dissociation energy of the PhO–H bond ($D_{O...H}$) may be regarded as the energy of the highest occupied molecular orbital (E_{HOMO}).[20-22] Consequently the change in the overall π-electron density at the oxygen atom (q_0) on going from one phenol to another, differing in the substituents, determines the differences in the dissociation energies of the O–H bonds in these phenols[23] and hence also the different capacities of the phenols to undergo oxidation. The effect of substituents is shown to the greatest extent when the substituent and the OH group are in the same conjugation system, i.e. are located in the *ortho*- or *para*-positions relative to one another[24,25]. The influence of the substituent in the *meta*-position is due solely to the inductive effect, since the conjugation effect of the *meta*-substituent is zero. Since the inductive effect decreases rapidly with distance[26], in the studies of the relative reactivities of sterically hindered phenols appreciable differences in reactivity may be expected in phenols having different substituents in the *para*-position.

Electron-donor substituents in the *para*-position increase the overall π-electron density at the oxygen atom[22], while electron-acceptor substituents decrease it. To characterise the capacity of the phenol for participation in a reaction involving the dissociation of the O–H bond, q_0 and E_{HOMO} will be used as the parameters of reactivity. Quantum-mechanical study of the activity of phenolic compounds as inhibitors of oxidation processes established a satisfactory correlation between the inhibiting activity of phenolic compounds and q_0 and E_{HOMO}.

Earlier it was established empirically that the activities of phenols as oxidation inhibitors are proportional to their redox potentials (v_0).[26,27] For certain stable phenol–phenoxy-radical systems, v_0 may be determined directly[27,29]; however, most of such systems are unstable under the conditions necessary for the determination of the potential. Fieser[30] proposed a method for the determination of v_0 of unstable redox systems, which consists in the determination of the potential of a stable redox system in the presence of the unstable system. In such cases one measures the minimum potential at which the rate of electron transfer from the phenol to the reference oxidant reaches a minimum value. This potential is called the "critical potential" v_c. For monohydric phenols, $v_c = v_0 - 0.136$ V, i.e. the critical potentials of the systems indeed characterise their redox potentials.

Calculations show the presence of a linear relation between the experimental criterion v_c of the capacity of phenols to be oxidised and the calculated reactivity parameter q_0 [20] and E_{HOMO}.[21] Hush[20] showed that $v_c = 3.0\,(q_0 - 1) - 0.55$ V. The highest occupied molecular orbital of the phenoxide ion is a non-bonding molecular orbital (NBMO), whose energy can be calculated from the formula

$$E_{HOMO} = \alpha + (c_{nx})^2 k_x \beta\,, \qquad (3)$$

where α and β are the coulombic integrals of the carbon atom and the resonance integral of the C=C double bond respectively, c_{nx} is the coefficient of the NBMO of the oxygen atom, and k_x the coulombic parameter of the oxygen atom. Fueno et al.[21] calculated $(c_{nx})^2$ for 200 phenols by the NBMO method. Comparison of the known values of v_c with $(c_{nx})^2$ revealed a linear relation between the two quantities (Fig. 1), which can be described by the equation:

$$v_c = 2.807\,(c_{nx})^2 - 0.459\,. \qquad (4)$$

Since β is negative and k_x is positive, it is evident from a comparison of Eqns. (3) and (4) that the NBMO becomes more stable when $(c_{nx})^2$ increases and the less stable is the NBMO the greater is the ease of oxidation of the phenol. Thus the capacity of the phenol to be oxidised can be estimated from the value of $(c_{nx})^2$, which is linearly related to v_c. Using this relation, the authors calculated v_c for about 180 phenols. In addition it has been shown that for phenols $D_{O...H} = v_c + 57$ kcal mole^{-1}, which made it possible to estimate the dissociation energies of O–H bonds for certain phenols[20].

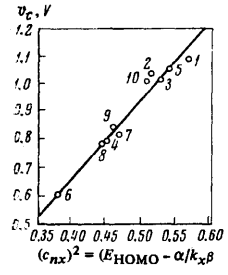
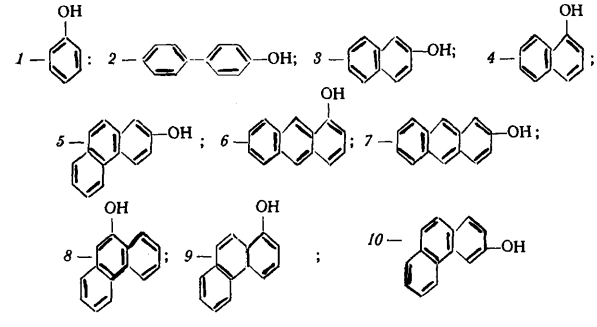


Figure 1. Variation of critical redox potentials of phenolic compounds with the energy of the highest occupied molecular orbital:

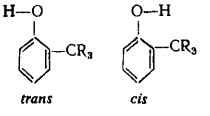


Another physicochemical quantity in which the dissociation energies of the bonds ruptured and formed in molecules of reactants and final products play a major role is the activation energy E_A. However, there is no exact correlation between E_A and bond dissociation energies, particularly in solutions, since effects associated with the electrostatic interaction between ions or dipoles and effects due to changes in solvation during the reaction are important for reactions in solution[31]. For this reason, the activation energies E_A cannot be used to estimate the relative reactivities. The determination of E_A is important for the study of the process mechanism (for example, in the determination of the rate-limiting stage or the changes in the mode of a complex process).

One of the important physicochemical characteristics of phenols dependent on the total π-electron density at the oxygen atom is the characteristic vibration frequency of the free hydroxyl ν_{OH}, which may be regarded as a measure of the polarity of the O–H bond[32]. The total π-electron density which has been increased, for example, by the introduction of electron-donor substituents in the *para*-position reduces the electronegativity of the oxygen atom and renders the coulombic integral of the σ-orbitals of oxygen more positive. This change in the coulombic integral then induces a change in the σ-electron structure of the phenol, particularly in the O–H bond[22], reducing the polarity of the latter[33]. Electron-acceptor substituents increase the

polarity of the O–H bond. The vibration frequency ν_{OH} increases with increasing bond polarity. However, experiments have shown[5,34,35] that the frequencies for phenols containing tertiary alkyl groups in the *ortho*-position are too high to be accounted for solely by their electron-donor properties. Thus, for *ortho*-substituted phenols, the average ν_{OH} is 3610 ± 2 cm^{-1}, for *ortho*-disubstituted phenols which do not contain two tertiary alkyl groups it is 3620 ± 2 cm^{-1}, and for phenols which do contain two such groups it is 3642 ± cm^{-1}.[35] Such powerful influence of tertiary alkyl groups in the *ortho*-position on ν_{OH} is due to two effects of these groups on the polarity of the O–H bond: in the first place the electron-donor effect and in the second the steric interaction of the tertiary alkyl groups with the hydroxyl, the O–H bond being coplanar with the benzene ring or nearly so[34,35]. Ingold's study of the infrared spectra of *o*-alkyl, *o*-t-alkyl-, and *o*-di-t-alkyl-phenols[34,35] showed that also other *o*-alkyl groups interact sterically with the hydroxyl, but this is restricted to the case where the OH group is oriented in the direction of the *ortho*-substituent.

According to Ingold[35,36], *o*-t-alkyl and *o*-alkyl-phenols exist in the form of two isomers corresponding to the *cis*- and *trans*-orientation of the hydroxyl relative to the *ortho*-substituent. Two bands have been observed in the infrared spectra of *o*-t-alkylphenols: the more intense band at the lower frequency corresponds to the *trans*-isomer and the less intense band at the higher frequency to the *cis*-isomer. These isomers have different properties. Thus, when the polarity of the solvent is varied, the *trans*-isomer behaves like phenol (with increasing polarity of the medium, ν_{OH} decreases appreciably), while the behaviour of the *cis*-isomer is similar to that of the corresponding 2,6-di-t-alkylphenol, which exhibits steric hindrance of the effect of the solvent[36,37].



Analysis of the half-width $\Delta\nu_{1/2}$ of the *o*-alkylphenol infrared band shows that the latter consists of two unresolved components. The fraction of the *cis*-isomer is determined by the bulk of the substituent in the *ortho*-position and also by the substituents in positions 5 and 6. In the *cis*-isomer there is steric repulsion between the phenolic hydrogen and the *ortho*-alkyl substituent, leading to an increase of frequency; in 2,6-di-t-alkylphenols there is a possibility of the interaction of the hydroxyl with the second t-alkyl group, reflected in the attraction of the unshared electron pairs of oxygen, which leads to a displacement of the absorption band towards longer wavelengths. These problems have been discussed in detail in Ingold's papers[35,36].

Attempts to use ν_{OH} as a criterion of reactivity were made in studies of the inhibiting activity of phenolic compounds. This criterion is based on the fact that the greater is the polarity of the O–H bond the greater is the displacement of the O–H band in the spectrum towards lower frequencies and the greater is the energy necessary for its homolytic dissociation and conversely. On this basis, it was to be expected that the inhibiting activity of a particular phenol can be assessed from the position of the free hydroxyl vibration band. Indeed comparison of the antioxidant activities and O–H bond polarities showed that the activity of monosubstituted phenol with different substituents in the *para*-position, expressed in terms of the ratio k_7/k_2 of the rate constants for the reactions

$$RO_2^{\cdot} + RH \xrightarrow{k_2} RO_2H + R^{\cdot},$$

$$RO_2^{\cdot} + C_6H_5OH \xrightarrow{k_7} RO_2H + C_6H_5O^{\cdot},$$

increases with ν_{OH}.[2] A rigorous linear relation between k_7/k_2 and ν_{OH} has been established[5] for phenols with substituents in the *ortho*-position, i.e. there is a proportional change in k_7/k_2 as ν_{OH} varies. However, for di- and trisubstituted phenols sterically hindered to different extents, there is a different relation. The efficiency of the inhibiting effect of phenols decreases with increasing ν_{OH} (Fig. 2). However, for phenols sterically hindered to the same extent there is again a possibility of a linear relation between k_7/k_2 and ν_{OH}.[5,38] Thus the use of ν_{OH} to estimate the relative reactivities is possible only within a series of phenols having similar steric structures. This is consistent with the results of the comparison of the inhibiting activities of phenols with the energies of the highest occupied molecular orbital[5]: the correlation curves for two groups of phenols (*o*-t-alkyl phenols and phenols without t-alkyl groups in the *ortho*-position) have different slopes.

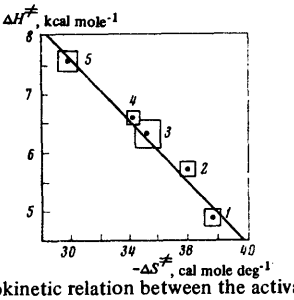


Figure 2. The isokinetic relation between the activation parameters: *1*) cyclohexane; *2*) benzene; *3*) chlorobenzene; *4*) anisole; *5*) benzonitrile.

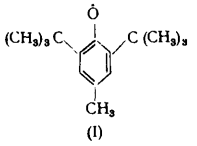
Table 1. Reactions of 2,6-di-t-butyl-4-R-phenols with peroxy-radicals.

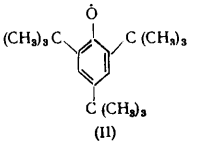
R	k_7, litre $mole^{-1}$ s^{-1} (styrylperoxy-radical) (Ref.39)	k_7/k_2 (tetralkyl-peroxy-radical) (Ref.5)	ν_{OH}, cm^{-1} (Ref.5)	ν_{OH}, cm^{-1} (Ref.38)	σ (Ref.24)
H	$2.35 \cdot 10^3$	967	3640	3648	0
CH_3	$7.95 \cdot 10^3$	1990	3643	3651	—0.17
t-C_4H_9	$7.3 \cdot 10^3$	1430	3642	3650	—0.20
OCH_3	$31.2 \cdot 10^3$		3652	3652	—0.27

However, within a series of phenols with the same steric hindrance, the changes in frequency are small. Thus, for a series of *para*-substituted phenols, the difference in frequency between the extreme members, with *p*-NO_2 (σ = +0.78) and *p*-OH (σ = −0.46) groups, amounts to 23 cm^{-1}, the resolution being 2–3 cm^{-1}.[5] The introduction of an alkyl substituent in the *para*-position of 2,6-di-t-butylphenol increases the inhibiting activity by a factor of more than two, while the change in frequency amounts to 2–3 cm^{-1} (Table 1). All this restricts the use of ν_{OH} as a reactivity index.

III. PROPERTIES OF PHENOXY-RADICALS—PRIMARY PHENOL OXIDATION PRODUCTS

Phenoxy-radicals are fairly stable. Their lifetimes depend on the structure of the radical, the polarity of the medium, and the presence of an oxidant in the system. In polar media the lifetimes of sterically hindered phenoxy-radicals are measured in fractions of a second[39], and therefore the ESR spectra of radicals generated in the oxidation of phenols in polar media, obtained by the usual steady-state technique, refer to secondary radicals[18,40,41]. On the other hand, in non-polar solvents the lifetimes of primary phenoxy-radicals are measured in minutes and even hours[42]. In the presence of an oxidant the primary phenoxy-radicals are converted into more stable secondary radicals[43]. If, for example, after the preparation of the radical (PbO_2 oxidant in an organic solvent) the excess PbO_2 is separated and the solvent is distilled off, the radical remains stable for several months[43]. The stability of sterically hindered phenols is determined by the steric hindrance and delocalisation of the unpaired electron over the benzene ring. The delocalisation of the unpaired electron is reflected in the infrared spectra of phenols. The 2.7 μm band associated with the O–H bond vibrations vanishes from the infrared spectra and a double bond, with frequencies similar to those of the vibrations of the C=O double bond conjugated with a C=C double bond appears in the region 6.0–6.4 μm.[44,45]. The delocalisation of the unpaired electron is confirmed by the analysis of the ESR spectra of phenoxy-radicals. The ESR spectrum of the free electron should have $g = 2.0013$ and comprise a single resonance line. The ESR spectra of phenoxy-radicals have a hyperfine structure (HFS), reflecting the distribution of the unpaired electron over the π-electron system of the phenoxy-radical. For example, the spectrum of 2,6-di-t-butyl-4-methylphenoxy-radical (I) consists of four triplets with the intensity ratios 1 : 3 : 1, the intensity ratios within each triplet being 1 : 2 : 1; the spectrum of 2,4,6-tri-t-butyl-phenoxy-radical (II) consists of a triplet with the intensity ratios 1 : 2 : 1.[42,44]


(I)


(II)

The appearance of four lines in the spectrum of compound (I) is due to the interaction of the unpaired electron with the three equivalent protons of the CH_3 group and the splitting of each line into three components by the interaction with the two equivalent protons in the *meta*-positions of the ring. The degree of interaction of the unpaired electron with β-protons is low, since the effect associated with the hyperconjugation overlapping of the orbitals falls sharply with distance and therefore usually the spectrum of compound (II) consists of a triplet due to the interaction with the metastable protons of the ring. The degree of interaction of the unpaired electron with the ring is characterised by the hyperfine splitting constant a_H, which can be calculated from the ESR spectrum. The observed splitting is proportional to the spin density ρ^π at the corresponding carbon atom. According to Mc Connel's equation, $a_H = Q\rho_C^\pi$. Assuming that Q_{CH}^H and $Q_{CCH_3}^H$ are 23.7 and 27.2 Oe respectively, Stone and Waters[39] calculated from the ESR spectra of phenoxy-radicals the distribution of electron density in the ring.

The data of Table 2 are in good agreement with the absolute values of ρ for the unsubstituted phenoxy-radical, quoted by Buchachenko[44]: $\rho_o = 0.29$, $\rho_m = 0.08$, $\rho_p = 0.45$. The spin densities calculated for theoretical models of these radicals differ significantly from those quoted above. The simplest model[46] represents the radical as a benzyl cation in which only five electrons are associated with the ring, the splitting constants a_{H_o} and a_{H_m} being then identical. A more complex model[47] yields $\rho_o = 0.32$, $\rho_m = 0.21$, and $\rho_p = 0.28$ for phenoxy-radicals. Taking into account the dipolar character of the C–O bond, the following distribution of spin density has been obtained for tri-t-butylphenoxy-radicals by semiempirical calculations[48]:

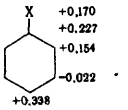


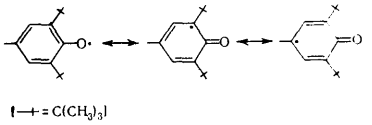
Table 2. Spin density of phenoxy-radicals[39].

Radical from	ρ_o	ρ_m	ρ_p	$\rho_p+2(\rho_o+\rho_m)$
Phenol	0.28	−0.075	0.42	0.83
p-Cresol	0.25	−0.06	0.44	0.82
2,6-Dimethylphenol	0.24	−0.07	0.40	0.74
2,4,6,-trimethylphenol	0.22	−0.06	0.44	0.76

The negative spin density in the *meta*-position implies that the direction of the spin of the unpaired electron at the *meta*-carbon atom is opposed to the direction of the spin of the radical as a whole[48,49]. Possibly the density at the C_1 atom is also negative; it has been suggested[48] that it is similar to the density at C_3 and C_5.

Despite such differences in experimental data, one can say that the major part of the unpaired electron is associated with carbon atoms C_2 and C_6, 20–25% being associated with the oxygen atom and C_1.[6,39,44,50].

Thus ESR spectroscopy of phenoxy-radicals demonstrates the existence of several reaction centres, which can be represented by three mesomeric structures in equilibrium[13]:

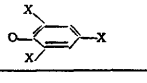

(5)

The reactivity of the reaction centres is determined by the electron density at the corresponding carbon or oxygen atom. This permits the prediction of the possible mode of oxidation reactions of phenols and of the nature and relative amounts of the products.

The introduction of substituents into the phenyl ring causes a redistribution of the electron density, which is reflected in a change of the splitting constants. Alkyl substituents reduce the splitting constants for the *ortho*- and *para*-positions, and alkoxy-substituents reduce the splitting constants for the *ortho*-position to a much greater extent than do alkyl substituents and also to a much greater extent than the constants for splitting by the *meta*-protons of the ring[39]. Probably a considerable proportion of the unpaired electron of such radicals is associated with two oxygen atoms. Table 3 presents the splitting constants for sterically hindered phenoxy-radicals[44]. The constant for splitting by *meta*-protons depends little on the alkyl substituent in the *para*-position, while the constant for splitting by the α-protons of the *para*-substituent has been

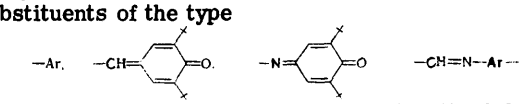
found to vary markedly with its structure. The replacement of methyl by t-butyl leads to a decrease of the constant by a factor of more than two[44]. For *para*- and *ortho*-alkyl-substituted unhindered phenoxy-radicals, the constant for splitting by α-protons decreases in the sequence $CH_3 > C_2H_5 > n\text{-}C_3H_7 \simeq C_6H_5CH_2 > iso\text{-}C_3H_7 > s\text{-}C_4H_9$.[37] A relation of this kind cannot be explained solely by a change in spin density ρ^{π}; it is probably also related to changes in the constants $Q^{H}_{C\text{-}Alk}$. The value of $Q_{C\text{-}H}$ for α-CH groups depends on the orientation of the C–H bond in relation to the electronic symmetry axis and hence also on the average conformations of CH_2R or CHR_2 in relation to the benzene ring[39,44]: the α-CH groups coplanar with the CH groups of the ring make a bigger contribution than the CH-groups oriented at a large angle with respect to the ring.

Table 3. Splitting constants of phenoxy-radicals (oersteds)[44].

	a_H(*meta*)	a_H(*para*)	Other nuclei
X=—CH_3	1.8	10.6	
—CH_2CH_3	1.8	8.7	
—$CH(CH_3)_2$	1.8	4.6	
—$CH_2C_6H_5$	1.8	—	0.37 (H in CH_3)
—$CH_2(C_6H_5)_2$*	1.6	8.7	
—$CH(C_6H_5)_2$	1.8	8.3	
—$CH(CH_3)C_6H_5$	1.8	6.6	
—CH_2OH	2.0	12.3	
—CH_2OCH_3	1.8	11.6	
—$CH_2N(CH_3)_2$	1.9	10.4	1.9(N)
—CH_2NH_2	1.8	11.0	1.8(N)
—NH_2	0.5	2.3	3.7(N)
—C(=O)H	2.5	—	
—C(=O)CH_3	2 2	—	
—C(=O)C_6H_5	1.9	—	
—C(=O)OCH_3	2.2	0.6	
—OCH_3	1.0	1.6	
—OCH_2CH_3	1.0	1.6	
—$OCH(CH_3)_2$	1.0	1 0	
—$OC(CH_3)_3$	1.0	—	
—OC(=O)CH_3	1.8	—	

* Error in Russian original (Ed. of Translation).

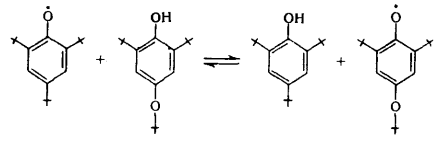
Buchachenko[44] made a thorough examination of the effect of the *para*-substituent on the splitting constants of sterically hindered phenoxy-radicals. The influence of the substituent can be explained by two factors: inductive and resonance effects. The inductive effect leads to a redistribution of the charges, which can lead to a change in spin density. The resonance effect implies the incorporation of the π-orbitals of the substituents in the general molecular orbital, resulting in a change of Q. At the same time there is a possibility of a redistribution of electron density. One can only put forward certain hypotheses concerning the effect of these factors on the splitting constants (see Table 15 in Buchachenko's book[44]). In a few cases one can speak of one or other effect predominating. Thus the increase in the stability of sterically hindered phenoxy-radicals on introduction into the *para*-position of substituents of the type



must be attributed to an increase in the length of the resonance conjugation chain, which favours greater delocalisation of the unpaired electron[43].

IV. FUNDAMENTAL REACTIONS OF PHENOXY-RADICALS: RECOMBINATION, ISOMERISATION, DISPROPORTIONATION, AND REACTION WITH OXYGEN

As already stated there are three reaction centres in phenoxy-radicals: the *ortho*- and *para*-carbon atoms and the oxygen atom. Only the *para*-carbon atom participates in the recombination reaction of sterically hindered phenoxy-radicals: the oxygen and *ortho*-carbon centres are blocked by bulky t-butyl groups. The capacity of 4-alkyl-2,6-di-t-butyl phenoxy-radicals for recombination is restricted by the bulk of the *para*-substituent: for example 2,4,6-tri-t-butylphenoxy- and 2,6-di-t-butyl-4-triphenylmethylphenoxy-radicals do not yield recombination products[44]. 4-Alkoxy-2,6-di-t-butylphenoxy-radicals exhibit higher stability in solution compared with alkyl derivatives. Direct comparison of the stabilities of 4-alkyl- and 4-alkoxy-2,6-di-t-butylphenoxy-radicals was achieved in experiments designed to investigate the equilibrium between phenoxy-radicals[9]. It was shown that the addition of a small amount of 4-butoxy-2,6-di-t-butyl phenol to a blue solution of 2,4,6-tri-t-butylphenoxy-radicals instantly results in the appearance of the red colour of 4-butoxy-2,6-di-t-butylphenoxy-radicals: on addition of a sufficient amount of 2,4,6-tri-t-butylphenol, the blue colour can be restored.



(6)

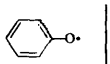
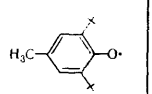
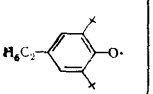
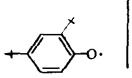
Spectrophotometric study of equilibrium (6) made it possible to estimate the equilibrium constant. The equilibrium constant for 4-butoxy-2,6-di-t-butylphenol at 25°C is 51.7 ± 4.1 and $\Delta H = -3.4 \pm 0.17$ kcal mole^{-1} and for 2,6-di-t-butyl-4-methoxyphenol $K = 210$ and $\Delta H = -5$ kcal mole^{-1}. Such a difference in the constant on going from 4-butoxy- to 4-methoxy-phenol can be accounted for by the fact that, on replacement of the methoxy-group by the butoxy-group, there is an increase in the polarity of the OH bond and therefore methoxyphenol is oxidised more rapidly. The constant for an equilibrium of this kind can be used in principle as a quantitative criterion of the capacity for oxidation but this is hindered by serious technical difficulties[9].

The recombination of 4-alkyl derivatives of phenoxy-radicals was investigated in detail by Land and Porter[51]. In the analysis of the electronic spectra of the photolysis product of phenols a characteristic group of bands (two or three) was observed in the region of 4000 Å; at longer wavelengths weak absorption was found. In their experiments involving the observation of the change in absorption at 4000 Å, Land and Porter investigated the kinetics of the decomposition of phenoxy-radicals. The results obtained are presented in Table 4.

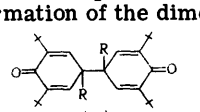
The decomposition of all the phenoxy-radicals investigated is a second-order reaction. The fact that the rate

constant is smaller by a power of ten than the calculated rate constant for a process the rate of which is controlled by diffusion suggests that the authors in fact observed dimerisation. 2,6-Di-t-butyl-4-methoxy- and 2,6-di-t-butyl-4-ethyl-phenoxy-radicals showed an interesting feature. These radicals initially disappear according to a second-order reaction and then, when the concentration of the radicals is still fairly high, the reaction deviates from the second order. Probably two processes are superimposed—rapid dimerisation [reaction (7)] and slow isomerisation.

Table 4. Rate constants for the initial decomposition of phenoxy-radicals by a second-order reaction at 20° ± 3°C. [51]

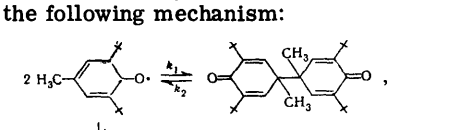
Radical	Solvent	k/ε, cm s^{-1}	k_1, litre $mole^{-1}$ s^{-1}; ε = 1800 max	$k_{calc} = \frac{8RT}{3000\eta}$, litre $mole^{-1}$ s^{-1}	K
	H_2O	$3\cdot10^5$	$5.4\cdot10^8$	$6.4\cdot10^8$	—
	CCl_4	$8.2\cdot10^4$	$1.5\cdot10^8$	$6.7\cdot10^8$	$7\cdot10^{-7}$
	CCl_4	$7.4\cdot10^3$	$1.3\cdot10^7$	$6.7\cdot10^8$	$1\cdot10^{-6}$
	liquid paraffin	$1.1\cdot10^4$	$2.0\cdot10^7$	$4.6\cdot10^7$	—

Neglecting the isomerisation process along the section of the curve which follows the second-order equation, one can determine the dimerisation constant k_1 and the equilibrium constant K, and the dimer dissociation constant k_2 (the final concentration of radicals was determined from the intensity of absorption and the initial concentration by extrapolation of the second-order curve to zero time). Comparison of the constants k_1 for methyl and ethylderivatives confirms the formation of the dimer (III):

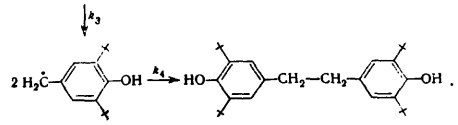


(III)

since on formation of a dimer with a different structure the *para*-substituent would have no steric effect. The slow isomerisation of the phenoxy-radical to a benzyl radical, with a rate constant k_3, is terminated by subsequent rapid dimerisation. Thus the process as a whole can be represented by the following mechanism:



(7)



(8)

Much work has been done on the isomerisation of phenoxy-radicals to benzyl radicals. The appearance of the intermediate benzyl radical makes it possible to explain the formation of 3,5,3′,5′-tetra-t-butylstilbene-4,4′-quinone (IV) in the oxidation of 2,5-di-t-butyl-4-methylphenol (V) with benzoyl peroxide[52]. The predominance (75% yield) of the stilbenequinone (IV) in the oxidation products (V) is observed also when other oxidants are employed[53,54]. Cook et al.[55] explained the formation of the benzyl radical as a result of the rearrangement of the primary phenoxy-radical and proposed the following oxidation mechanism:

$$\text{phenol} \rightarrow \text{phenoxy-radical} \xrightarrow[\text{(rearrangement)}]{} \text{benzyl radical} \xrightarrow[\text{(dimerisation)}]{} \text{final products.} \quad (9)$$

This mechanism can now be regarded as proved. The application of the ESR method in the study of the oxidation showed that the primary radical produced in the oxidation of compound (V) is 2,6-di-t-butyl-4-methylphenoxyl (I).[56] The study of the kinetics of the oxidation of sterically hindered phenols by the ESR method[57] revealed that the kinetic curve for the disappearance of radicals derived from 2,6-di-t-butyl-4-methyl- and 2,6-di-t-butyl-4-ethyl-phenols distinctly follows a first-order process, which suggests that the rate-limiting stage in the oxidation of these phenols is intramolecular rearrangement of the phenoxy-radical to a benzyl radical. Table 5 shows that in a polar solvent the isomerisation rate constant is markedly reduced. This may be due to the solvation of the phenoxy-radical. It has been noted[58,59] that solvation leads to the delocalisation of the unpaired electron over the solvent shell.

Table 5. Kinetic data on the oxidation of sterically hindered phenols in various media[57].

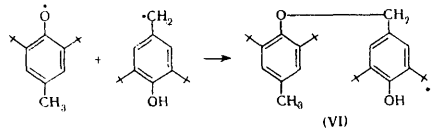
Phenol	Solvent	k, s^{-1}; t = 25°C	E, kcal $mole^{-1}$	k_0, s^{-1}
2,6-Di-t-butyl-4-methylphenol	benzene	$1.33\cdot10^{-2}$	11.4	$3.1\cdot10^8$
	methylcyclohexane	$1.23\cdot10^{-2}$		
		$0.35\cdot10^{-2}$		
2,6-Di-t-butyl-4-ethylphenol	benzene	$0.75\cdot10^{-2}$		

The low value of k_0 can be explained by the fact that in the intramolecular rearrangement the bulky substituent prevents the formation of a π-complex between the migrating group and the ring. However, the temperature range in which the reaction was studied has not been indicated[57].

According to the data of Brodskii and coworkers[60], the disappearance of 2,6-di-t-butyl-4-ethylphenoxy-radicals is a first-order reaction only close to room temperature. On increase of temperature, the first order is gradually replaced by the second. At room temperature the rearrangement of the phenoxy-radical to a benzyl radical in fact determines the nature of the process. The occurrence of the intramolecular rearrangement has been demonstrated directly by the oxidation with PbO_2 of 2,6-di-t-butyl-4-methylphenol deuteriated at the hydroxy-group, in solution not containing mobile protons[61]. The oxidation leads to a product the infrared spectrum of which contains a band with ν_{OH} = 3647 cm^{-1}, while ν_{OD} for the initial phenol is 2692 cm^{-1}.[62] On the other hand, the oxidation of 2,6-di-t-butyl-4-methylphenol deuteriated in the CH_3 group results in the appearance of a 2692 cm^{-1} band in the infrared spectrum of the product. The replacement of OD by OH and conversely is possible only when the

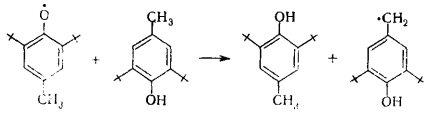
phenoxy-radical rearranges to a benzyl radical. On increase of temperature, the disproportionation reaction begins to make a significant contribution.

On the basis of the above mechanism, it would appear that the product of the cross recombination of the phenoxy- and benzyl radicals should be expected in the reaction products:



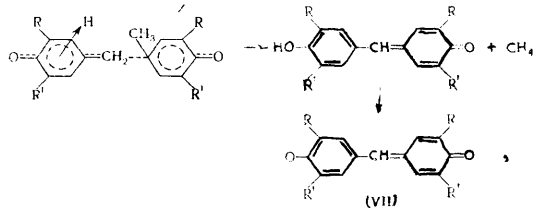
(VI) (10)

However, compound(VI) was not detected. Bennett[57] explained the absence of the product of cross recombination of the phenoxy- and benzyl radicals by the low rate of interaction of phenoxy-radicals with other free radicals[63]. One can add to this that the reaction at the oxygen atom is in general not characteristic of sterically hindered phenoxy-radicals, with the exception of the proton transfer reaction (the reaction with hydrocarbons[64,65], with another molecule of the same compound[66], and with oximes and hydroperoxides[67]). In the reaction between the phenoxyl and another radical the addition takes place as a rule in the *ortho*- or *para*-position. The benzyl radical may be regarded as a variety of alkyl radicals which are known to add to phenoxy-radicals (in the inhibition of the polymerisation of styrene for example) in accordance with the general rule, the addition to the oxygen atom with formation of an ether occurring only partially[44,45]. Apparently the absence of the cross recombination product cannot be regarded as a criterion in the assessment of the oxidation mechanism, as was suggested earlier[40]. The formation of the benzyl radical by reaction (11) is also unlikely[40]:

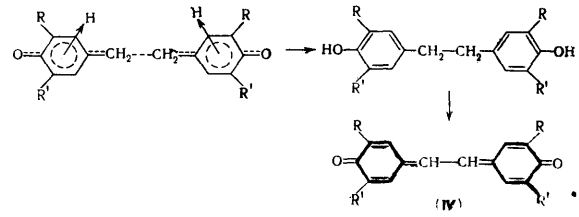


(11)

since the reaction of 2,4,6-tri-t-butylphenoxy-radicals with toluene, which has a similar mechanism, takes place at a low rate, the activation energy for such a reaction amounting to 23 kcal mole^{-1} and $k_0 = 9.7 \times 10^{-13}$ cm^3 s^{-1}.[65] In this case the independence of the rate constant of the initial phenol concentration may be regarded as direct proof. However, in the literature there are only Bennett's data[57], which show that the initial concentration varied within a 5% range. The range of variation of concentration is in this case too narrow to conclude that the rate constant for the disappearance of 2,6-di-t-butyl-4-methylphenoxy-radicals is independent of the concentration of phenol. Becconsall et al.[40] put forward the following mechanism to account for the appearance of compound (VII) among the reaction products:

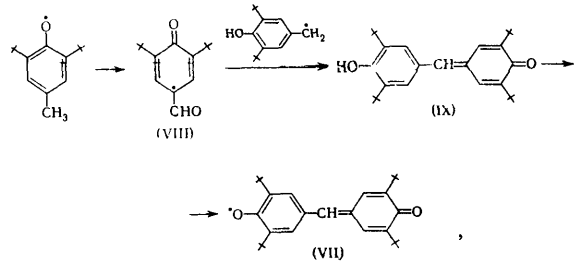


(VII) (12)



(IV)

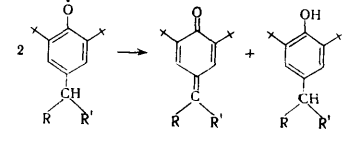
This mechanism does indeed account for the formation of compound (VII), which was detected by Coppinger[68], but it is difficult to accept it since it contradicts the first-order of the radical disappearance reaction, which has been firmly established[57,59]. It can be supposed that the formation of radicals (VII) is preceded by the oxidation of the phenoxy-radical, for example with formation of compound (VIII). The subsequent removal of the *para*-substituent as a result of the interaction of compound (VIII) with the benzyl radical,



(VIII) (IX) (VII) (13)

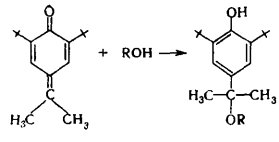
leads to the phenol (IX), whose further oxidation results in the formation of the radical (VII).

A characteristic reaction in the absence of oxygen of sterically hindered phenoxy-radicals with a *para*-substituent containing a tertiary α-hydrogen atom is disproportionation with formation of the corresponding quinone methide and the initial phenol[45,69]:



(14)

A detailed study has been made of the properties of 2,6-di-t-butyl-4-isopropylidene-2,5-cyclohexadien-1-one the reduction of which with lithium aluminium hydride results in the regeneration of the initial phenol and its reduction with zinc in acetic acid leads to the dimeric product 1,2-bis-(3,5-di-t-butyl-4-hydroxyphenyl)-1,1′,2,2′-tetramethylethane. In the presence of an alcohol the acid-catalysed reaction (15) takes place:

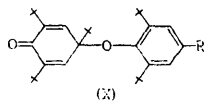


(15)

The phenols formed give rise to radicals, the stability of which is similar to that of the 2,4,6-tri-t-butylphenoxy-radical.

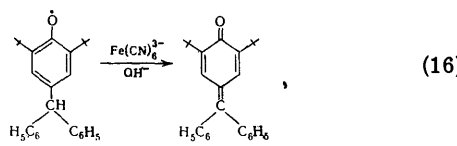
The disproportionation reaction of 2,4,6-tri-t-butylphenoxy-radicals exhibits certain characteristic features[70]. The products of this reaction are 2,4,6-tri-t-butylphenol and at least two dimeric products. Elemental analysis

and the ultraviolet and infrared spectra of one of these dimers suggest the structure (X):

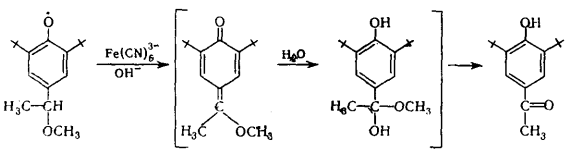


(X)

The behaviour of phenoxy-radicals containing $(C_6H_5)_2CH$ or $CH(CH_3)OCH_3$ groups in the *para*-position is interesting; the oxidation of the initial phenols is accompanied by disproportionation or, in the presence of an excess of alkaline hexacyanoferrate(III), by decomposition according to reactions (16) and (17) respectively:



(16)



(17)

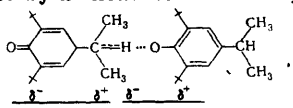
The kinetics of the disproportionation reaction were investigated for a series of sterically hindered phenoxy-radicals differing in the *para*-substituent [71]. The disappearance of the radicals was followed from the decrease of the optical density at 630 nm (phenoxy-radicals absorb in the visible region). Analysis of the kinetic curve shows that the reaction is of second order with respect to the radicals. Comparative studies of a number of phenoxy-radicals demonstrated that the rate of disproportionation decreases for the following series of substituents: $CH_3 > C_2H_5 >$ iso-C_3H_7 > cyclohexyl > s-C_4H_9 (this might have been expected bearing in mind the increasing bulk of the substituent in this series). The activation energy for the reaction increases in the sequence iso-C_3H_7 < s-C_4H_9 < cyclohexyl. The activation parameters were calculated from the results (Table 6).

Table 6 shows that the disproportionation rate constant for the 2,6-di-t-butyl-4-isopropylphenoxy-radical changes little on going from one solvent to another. However, this is not due to the absence of interaction with the solvent

Table 6. Rate constants and activation parameters for the disproportionation reaction [71].

Radical	Solvent	k, litre mole^{-1} s^{-1}; 25°C	E, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1} 25°C	$\Delta S^{\neq}$, kcal mole^{-1} deg^{-1}
2,6-Di-t-butyl-4-isopropyl-phenoxyl	benzene	2.17±0.01	6.23±0.15	5.74±0.14	−37.80±0.50
	cyclohexane	3.82±0.09	5.50±0.18	4.91±0.16	−39.46±0.59
	anisole	3.20±0.03	7.20±0.14	6.61±0.13	−34.12±0.46
	benzonitrile	5.64±0.3	8.16±0.19	7.57±0.19	−29.26±0.63
	bromobenzene		7.25±0.11	6.76±0 10	
	chlorobenzene	3.08±0.08	6.94±0.25	6.35±0.23	−35.06±0.82
	carbon tetrachloride		5.80±0.09	5.21±0.08	
4-s-Butyl-2,6-di-t-butyl-phenoxyl	benzene	0.618±0.015	7.04±0.11	6.45±0.10	
2,6-Di-t-butyl-4-cyclohexyl-phenoxyl	benzene	1.28±0.029	7.93±0.14	7.34±0.13	
	cyclohexane		7.45±0 11	6.83±0.10	

but to the presence of a compensation effect with an isokinetic temperature of −9°C, as shown by the linear relation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for various solvents (Fig. 2). The authors explain this effect by the different degrees of solvation of the reaction and transition states; the latter can be represented by a "head-to-tail" complex:



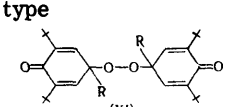
The formation of the transition state is accompanied by desolvation. Close to the isokinetic temperature, a linear relation between the rate constant (and hence also the free energy of activation) and the dielectric constant of the solvent cannot be observed. At temperatures differing significantly from the isokinetic temperature, the difference in the dipole neutralisation energy in the "head-to-tail" orientation in two media with different dielectric constants D_1 and D_2 is defined by the formula

$$\Delta E = \frac{28.9\mu_A \mu_B \Delta D}{D_1 D_2 r^2},$$

where μ_A and μ_B are the dipole moments of the two dipoles and r is the difference between them. Near the isokinetic temperature a not entirely rigorous (large scatter) linear relation between $\Delta H^{\neq}$ and $(D-1)/D$ is observed in this case, in agreement with the results of Leffler and Alder [72]. Thus the results indicate the possibility of a polar factor in radical reactions.

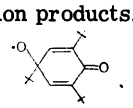
As already stated for 2,6-di-t-butyl-4-methylphenol, in the presence of an oxidant the spectrum of the primary radical varies in time. Table 7 presents the parameters of the spectra of primary and secondary phenoxy-radicals obtained in the oxidation of a number of phenols with PbO_2 in cyclohexane in the absence of oxygen [42]. The primary radical derived from compounds having an α-methylene group is replaced by a more stable secondary radical, which is formed from the primary radical as a result of the oxidation of the *para*-substituent. The spectrum of such a secondary radical consists of a triplet with a_H = 1.2 Oe, which suggests that the splitting is due to the equivalent *meta*-protons.

The presence of oxygen leads as a rule to the formation of peroxides of the type



(XI)

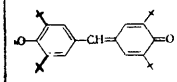
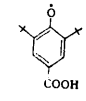
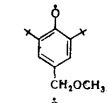
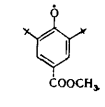
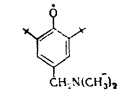
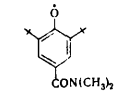
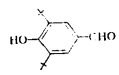
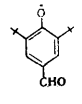
where R = alkyl, alkoxy-group, C_6H_5, C_6H_5CO, etc. [40,44,45,73] The study of the properties of quinolide peroxides showed that the peroxide derived from the 2,4,6-tri-t-butylphenoxy-radical decomposes, at 100–120°C for example, with formation of unstable radicals [40,44], the spectra of which consist of a triplet with a_H = 1.2 Oe. It is believed that the breakdown of the peroxide takes place at the O–O bond with formation of a radical with structure (XII); 2,6-di-t-butylbenzoquinone and isobutene have been detected in the decomposition products.



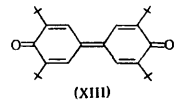
(XII)

A comparative study of the reaction of phenoxy-radicals with oxygen has been made for a series of radicals obtained by the oxidation of the corresponding phenols with alkaline potassium hexacyanoferrate(III). [70] The reaction rate was estimated from the disappearance of the colour of the radical. It was shown that the rate of disappearance of the

Table 7. ESR spectra of phenols undergoing oxidation[42] (oxidant—PbO_2 in cyclohexane).

Phenol	Description of spectrum	Time of observation	Splitting constants, Oe					Radical
			o-methylene group	m-methylene group	p-methylene group	ring H	others	
	(a) quartet of triplets	immediately	—	—	10.7	1.8	—	
	(b) triplet	after 10 min	—	—	—	1.3	—	
	(c) doublet of quintets	after several days	—	—	—	1.4	5.9	
	(a) triplet of triplets	immediately	—	—	9.0	1.8	—	
	(b) triplet		—	—	—	1.2	—	
	(a) triplet of triplets	immediately	—	—	12.3	2.0	—	
	(b) triplet		—	—	—	1.25	—	
	(a) triplet of triplets	immediately	—	—	11.6	1.8	—	
	(b) triplet		—	—	—	1.2	—	
	(a) triplet of quintets	immediately	—	—	10.4	1.9	1.9	
	(b) triplet		—	—	—	1.2	—	
	(a) triplet	immediately	—	—	—	1.3	—	
	(a) triplet	immediately	—	—	—	1.8	—	

colour decreases in the following series of *para*-substituents: $t\text{-}C_4H_9 > C_6H_5 > (C_6H_5)_3C > C_6H_5CO > CN$. On going from C_6H_5 to CN, the rate decreases by a factor of ten, while on going from C_6H_5 to $t\text{-}C_4H_9$ it increases by a factor of ten. Such reduction of sensitivity with respect to oxygen can be due to enhanced resonance stabilisation or partial lowering of electron density at the *p*-carbon atom. Analysis of the oxidation products revealed an appreciable yield of biscyclohexadienone peroxides when the groups C_6H_5 and C_6H_5CO are located in the *para*-position. The oxidation of 2,6-di-t-butyl-4-nitrophenol and 3,5-di-t-butyl-4-hydroxybenzoic acid leads to the formation of the dimeric product (XIII), which is characteristic of the oxidation of 2,6-di-t-butylphenol[17].

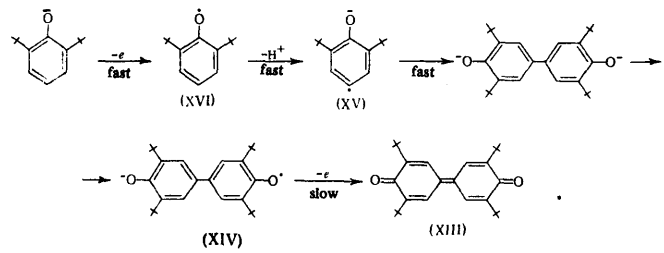


(XIII)

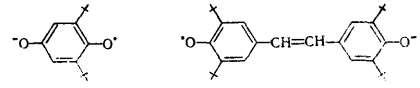
V. OXIDATION OF STERICALLY HINDERED PHENOLS BY MOLECULAR OXYGEN IN POLAR MEDIA

So far we have discussed the reactions of phenoxy-radicals obtained by the homolytic oxidation of phenols in the absence of oxygen. The oxidation of phenols with molecular oxygen in an alkaline medium shows certain characteristics features. In the first place the study of the oxidation by the ESR method revealed the presence of radicals of the semiquinone type and in the second place the kinetic oxygen absorption curve is of an autocatalytic type. Finally, analysis of the molecular oxidation products showed the presence of hydroperoxides and their decomposition products (quinols).

We shall consider the ESR study of the oxidation of the simplest representative of sterically hindered phenols—2,6-di-t-butylphenol[17]. Its oxidation product in an alkaline medium is dibenzoquinone (XIII). If alcoholic potassium hydroxide is added to a tube containing an alcoholic solution of phenol saturated with air and the tube is closed to prevent further diffusion of oxygen and placed in the resonator of a radiospectrometer, the ESR spectrum of this system shows in the first minutes a broad singlet with increasing intensity, which is subsequently split into a quintet with intensity ratios of 1 : 4 : 6 : 4 : 1 and a splitting constant of 0.6 Oe; the 5-line spectrum then disappears and a triplet remains with intensity ratios of 1 : 2 : 1 and a_H = 1.5 Oe. The triplet spectrum persists for several hours. The broad singlet line is probably due to the 2,6-di-t-butylphenoxy-radical (a 6-line spectrum with intensity ratios of 1 : 1 : 2 : 2 : 1 : 1 is expected) and almost simultaneously a radical forms which gives rise to a quintet. The quintet spectrum can be attributed to the radical-ion (XIV), since an identical spectrum arises in the reduction of dibenzoquinone (XIII). The triplet spectrum can be attributed to 2,6-di-t-butyl-4-benzosemiquinone. A radical of this kind can form from the intermediate hydroperoxide. The triplet splitting may be due also to the radicals (XV), which form from the phenoxy-radicals when the number of protons available is insufficient. The existence of the (XVI)–(XV) stage can be postulated also on the basis of the fact that in the oxidation of phenol with neutral potassium permanganate in acetone there appears initially a broad singlet line, which then splits into a quintet. Analysis of the spectrum suggests the following mechanism for the oxidation:

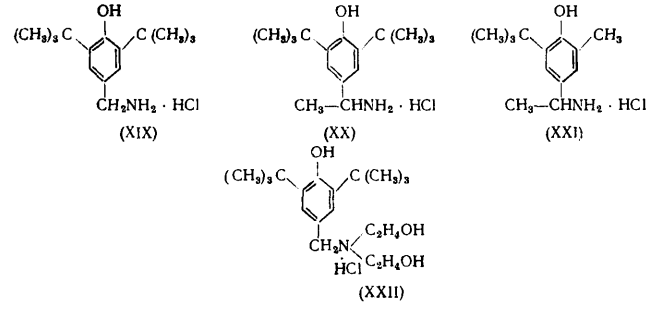


In the oxidation of 2,6-di-t-butyl-4-methylphenol (ionol) with air in alkaline acetone a radical forms whose ESR spectrum consists of eight lines[18]. In the presence of a deficiency of oxygen the 8-line spectrum disappears and is replaced by a triplet with a splitting of 1.3 Oe and intensity ratios of 1 : 2 : 1. This spectrum may be due either to the radical (XVII) or to the radical (XVIII)[40]. A triplet of this kind was observed after three days in the oxidation of ionol in alkaline methanol; the initial spectrum consists of fifteen lines and appears to result from the superposition of the spectra of several radicals[40]. The present authors'[41] study of the oxidation of four 4-aminoalkyl-2,6-di-t-butylphenols (XIX)–(XXII) in alkaline aqueous alcoholic (1 : 1) solution saturated with oxygen showed that, for all four phenols, which differ in the *para*-substituent, the reaction mixture has a yellow-green colour and even in the first minute gives rise to an ESR signal in the form of a triplet with a splitting of 1.4 Oe and intensity ratios of 1 : 2 : 1.[42] The structure of this spectrum persists for tens of minutes at 45–67 °C. The kinetic curve of the radical with a triplet ESR spectrum passes through a maximum, the descending branch representing the disappearance of the radicals. Most of the curve can be formally described by the equation for first-order kinetics.



(XVII), a_H = 1.5 Oe (XVIII), a_H = 1.6 Oe

The radicals generated in the oxidation of phenols (XIX), (XX), (XXI), and (XXII) disappear with the same activation energy (23 kcal mole^{-1}).



(XIX) (XX) (XXI)

(XXII)

All these findings confirm that we are dealing with the same radical in all four cases and that this radical is not a primary phenoxyl. The spectra of primary phenoxy-radicals derived from these phenols should show significant differences. Thus the primary phenoxy-radical from 4-aminomethyl-2,6-di-t-butylphenol (XIX) obtained in the oxidation of this phenol with PbO_2 in benzene has an ESR spectrum in the form of a triplet of quintets with a splitting of 10.4 Oe in the triplet and 1.9 Oe in the quintet[43], while

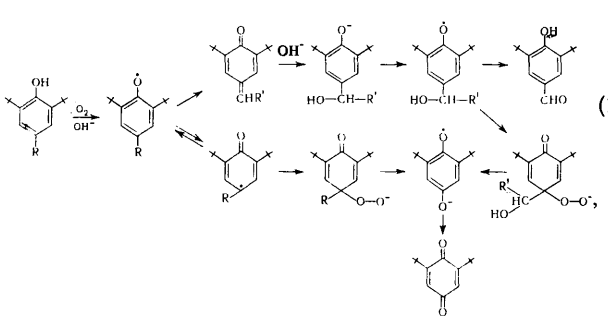
the spectrum of the phenoxy-radical from 4-aminoethyl-2,6-di-t-butylphenol (XX) should consist of a doublet of quintets with a splitting of about 8.5 Oe in the doublet and 1.8–1.9 Oe in the quintet.

The spectrum obtained by the authors can be attributed to 2,6-di-t-butyl-1,4-benzosemiquinone (XVII). The absence of splitting by *ortho*-substituents under these conditions leads to identical spectra of the semiquinone radical-ions derived from 4-aminoethyl-6-t-butyl-2-methylphenol (XXI) and phenols containing two t-C_4H_9 groups in the *ortho*-positions.

The radical detected by Adams et al.[17] and Becconsall et al.[40] in the oxidation of ionol in a polar medium, which has a triplet spectrum with a splitting 0.1 Oe, is also 2,6-di-t-butyl-1,4-benzosemiquinone (XVII). We have shown[74] that the formation of 2,6-di-t-butyl-1,4-benzosemiquinone is characteristic of the oxidation with molecular oxygen in alkaline aqueous alcoholic solution of 2,6-di-t-butylphenols containing electron-donor substituents in the *para*-position. The oxidation of alkylphenols with oxygen in alkaline aqueous alcoholic solution probably begins with the stage involving the formation of the corresponding phenoxy-radicals, which are extremely unstable under the experimental conditions and can either disproportionate to the corresponding methylenequinones or interact with oxygen to form 2,6-di-t-butyl-1,4-benzosemiquinone, which leads as a rule to the removal of the *para*-substituent regardless of the structure of the initial 4-substituted 2,6-di-t-butylphenol.

In our experiments on the oxidation of certain 4-substituted phenols, quinone methides stable in an alkaline aqueous alcoholic solution were also isolated. Such methides are 2,6-di-t-butyl-4-*NN*-dimethylaminomethylenecyclohexa-2,5-dien-1-one and 2,6-di-t-butyl-4-methoxymethylenecyclohexa-2,5-dien-1-one, which are converted under the action of acid into 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXIII). This benzaldehyde was also detected in the oxidation products of 2,6-di-t-butyl-4-(β-hydroxyethyl)aminophenol (XXII) on addition of concentrated hydrochloric acid to the reaction mixture. The formation of quinone methides in the reaction is confirmed also by the ultraviolet spectra of the reaction mixture. The absorption by the reaction mixture obtained from 2,6-di-t-butyl-4-dimethylaminomethylphenol in the region of 340 nm is due to aminomethylenequinone[75]; 2,6-di-t-butyl-4-methoxymethylenecyclohexa-2,5-dien-1-one gives rise to an absorption band with a maximum at 325 nm.

2,6-Di-t-butyl-1,4-benzosemiquinone (XXII) is formed from an intermediate hydroperoxide with a *para*-quinolide structure. On the basis of the results of Strigun et al.[41,74] and other literature data, the oxidation with molecular oxygen in polar media of alkylphenols with electron-donor substituents in the *para*-position can be represented by the following mechanism:

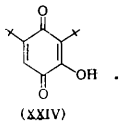


(18)

where R = CH_3, C_2H_5, $CH(CH_3)_2$, CH_2OCH_3, $CH_2OC_2H_5$, CH_2NH_2, $CH_2N(CH_3)_2$, $CH_3-CH(CH_2)$, or $CH_2N(CH_2CH_2OH)_2$.

The relative amounts of reaction products depend on reaction conditions. 3,5-t-Butyl-4-hydroxybenzaldehyde formed during the reaction is not oxidised by oxygen under the experimental conditions and does not interact with any of the other reaction products and therefore the mode of the disproportionation reaction of the phenoxy-radical can be assessed from the amount of the hydroxy-aldehyde. When the concentration of oxygen in the system is sufficiently high, the phenoxy-radicals are rapidly converted into semiquinone radical-ions. As a result, the oxidation process is determined by the characteristics of the oxidation of the semiquinone. According to the above mechanism, semiquinone radicals disappear in the disproportionation reaction, which leads to the formation of quinone in the system. At advanced stages of the reaction the quinone accumulated in the system is reduced. The formation of semiquinone by the reduction of the quinone in the alkaline medium[76,77] is superimposed on the disproportionation process, as a result of which the kinetic curve describing the disappearance of the radicals is of a complex form and cannot be fully described by simple equations.

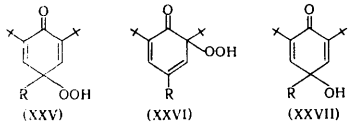
The hydroxy-quinone with the structure (XXIV) has been detected in the oxidation products of the phenol (XXII)[74], its structure having been demonstrated by infrared, ESR, and NMR spectra. It has been shown that this hydroxy-quinone is formed on direct interaction between 2,6-di-t-butyl-1,4-benzoquinone and alkali. All these findings indicate that, at advanced stages of the reaction, the system containing a phenol undergoing oxidation obeys the general laws governing the reduction of quinones[74,76,77].



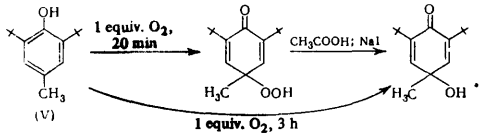
(XXIV)

Hydroperoxides with structures (XXV) and (XXVI) are characteristic products of the oxidation with molecular oxygen of sterically hindered phenols[78–80]. In an alkaline solution they isomerise and decompose into the quinols (XXVII) or the initial phenol.

The absorption of one equivalent of oxygen by a solution of ionol (V) in alkaline ethanol leads to the formation of the hydroperoxide (XXV) with a yield of 86%.[78] Slow absorption (restricted access of the gas) of the same amount of oxygen results in the formation of the corresponding quinol[19]:



(19)



The oxidation of 2,4,6-tri-t-butylphenol under similar conditions yields the *o*-hydroperoxide as the main product together with a small amount of *p*-hydroperoxide. The properties of these hydroperoxides are interesting[79]. The reduction of *p*-hydroperoxides with hydrogen iodide leads to the corresponding quinols. When the *p*-hydroperoxide (XXV, R = C_4H_9) is heated for 2 h at 40°C and pH 14 in

alcohol in the presence of oxygen, the isomeric *o*-hydroperoxide (XXVI, R = C_4H_9) and the corresponding quinol (XXVII, R = C_4H_9) are formed. Under the same conditions the *o*-isomer gives rise to the *p*-hydroperoxide and the corresponding quinol but the relative amounts of the two products are different (Table 8).

Table 8. Isomerisation of hydroperoxides (XXV) and (XXVI) (R = t-C_4H_9.[75]

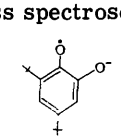
Hydroperoxide	% formed on heating		isomer / quinol
	of isomer	of quinol	
p-Hydroperoxide	19.5	30.5	0.64
o-Hydroperoxide	21	29	0.72

Table 8 shows that the isomerisation is accompanied by the decomposition of the hydroperoxide. It has been shown that when the *p*-hydroperoxide (XXV, R = CH_3) is heated under the above conditions for 4 h, it is decomposed to the extent of 80%, the main product being the quinol (XXVII, R = CH_3); heating in nitrogen leads to the decomposition of the peroxide to the extent of 90%, the reaction products—quinol (XXVII) and ionol—being formed in proportions of 2 : 3. On decomposition in a stream of nitrogen, the yield of the phenol and oxygen can reach 70%. The study of this reaction in 50% aqueous t-butyl alcohol[80], with potassium cyanide added to bind heavy metal ions which catalyse the decomposition of the peroxide, showed that the decomposition is a first-order reaction and depends on the pH of the medium. This suggested that the reaction proceeds as follows:

$$ROO^- \rightarrow R^- + O_2 \,. \qquad (20)$$

The *p*-hydroperoxide (XXV, R = C_4H_9) undergoes a similar reaction, but the yield in this case is lower.

The ESR study[78] of the decomposition of the *p*-hydroperoxide (XXV, R = CH_3) in an alkaline medium showed that after heating for 4 h in the system gives rise to the characteristic spectrum of the catechol semiquinone (XXVIII); the presence of isobutene was demonstrated by gas–liquid chromatography and mass spectroscopy.



(XXVIII)

When equimolar amounts of solutions of the *p*-hydroperoxide (XXV, R = CH_3) and ionol or of cumenyl hydroperoxide and the quinol (XXVII, R = CH_3) are mixed, this type of spectrum appears instantly. The characteristics of the spectra of these semiquinones are presented in Table 9.

Gersmann and Bickel[80,81] suggested that the *o*-quinone or *o*-semiquinone radical-ions formed in the decomposition of *o*-hydroperoxides can catalyse the oxidation of phenols. The data of Conradi and McLaren[82] demonstrate that the *o*-quinone is definitely formed in the oxidation of phenols. Gersmann and Bickel made a detailed study of the kinetics of the oxidation of sterically hindered phenols in polar media[80,81]. The kinetic oxygen absorption curve is of an autocatalytic type. The authors explained the autocatalysis of the oxidation of sterically hindered phenols by the catalytic effect of the *o*-hydroperoxide (Fig. 3); *p*-hydroperoxides do not exhibit a catalytic effect. The catalytic effect of the *o*-hydroperoxide is in all probability associated with its decomposition accompanied by the formation of the active catalyst: *o*-quinone or a radical. The attempts to show that the auto-oxidation of sterically hindered phenols in polar media with molecular oxygen is a radical chain process proved unsuccessful: the addition of hydrogen donors (9,10-dihydroanthracene) and initiators ($\alpha\alpha$-azobisisobutyronitrile) did not show a definite effect on the rate of oxidation; the addition of free-radical reaction inhibitors (quinones and aromatic polynitro-compounds) accelerates the oxidation. This favourable catalytic effect will be discussed in detail below.

Table 9. Properties of the ESR spectra of *o*-semiquinones observed in the oxidation of 2,6-di-t-butyl-4-R-phenols.

R	Intensity ratio	Splitting constants	
		a_1	a_2
CH_3	1:1:3:3:3:3:1:1	5.2	2.5
Benzyl	1:1:2:2:1:1	4.1	2.5
iso-C_3H_7	1:2:1	2.4	2.4
t-C_4H_9	1:1		2.5

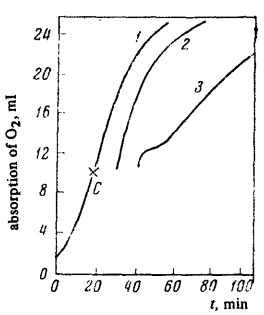


Figure 3. Auto-oxidation of 2,4,6-tri-t-butylphenol: *1*) phenol alone, initial concentration 4 x 10^{-2} M; *2*) phenol mixed with the *o*-hydroperoxide in proportions corresponding to the content of both components in the reaction mixture at point *C*; *3*) phenol alone, initial concentration equal to the concentration of the phenol in the reaction mixture at point *C*.

Comparative study of the auto-oxidation of sterically hindered phenols in various solvents showed that oxidation in the 1 : 1 mixture of t-butyl alcohol and 1,2-dimethoxyethane containing potassium butoxide is much faster than in 90% ethanol; the kinetic [oxygen] absorption curve does not show an induction period in this case, but the yield of hydroperoxide in ethanol is higher. The reaction remains of first order with respect to the phenoxide ion up to 80% conversion; at the same concentration of alkali the reaction is of first order with respect to oxygen pressure. Table 10 presents data on the oxidation of ionol.

The much higher rate of oxidation in the presence of potassium t-butoxide in the t-butyl alcohol–1,2-dimethoxyethane mixture is due to the fact that in this solution the phenol is evidently completely ionised while in 90% ethanol

at pH 13 ionol is dissociated only to the extent of 20%. Furthermore, the difference in solvation may play a significant role. The formation of hydrogen bonds is in this case difficult due to steric hindrance. The importance of the size of solvent molecules can be seen from the low rate of oxidation in 100% methanol containing potassium methoxide.

Table 10. Auto-oxidation of ionol (0.5 - 1.0 mole/30 ml).[81]

№	Molarity of base	Solvent*	p_{O_2}, mmHg	t, °C	k, min^{-1}
1	0.10	A	76	25	0.92
2	0.10	A	76	0	0.12
3	0.25	A	76	0	0.12
4	0.25	A	53	0	0.075
5	0.25	A	34	0	0.052
6	0.10	A	76	0	0.644
7	0.10	A	76	0	0.253
8	0.10	90% C_2H_5OH	76	0	0.0024
9	0.10	100% CH_3OH	76	0	0.0005

* A represents a 1 : 1 mixture of t-butyl alcohol and 1,2-dimethoxyethane; in experiment No. 6 20 mg of 2,6-di-t-butylbenzoquinone and in experiments Nos. 7 and 8 20 mg of *m*-dinitrobenzene were added.

As stated above, 2,6-di-t-butylbenzoquinone, duroquinone, and *m*-dinitrobenzene proved to be effective catalysts of the oxidation of sterically hindered phenols (Table 11). The study of the kinetics of the catalysis by quinones and polynitrobenzenes showed differences which the authors attributed to differences in the mechanism of the catalysis. Thus the oxidation catalysed by *m*-dinitrobenzene depends on the concentration of the catalyst, is of first order with respect to the phenol (as shown by the analysis of the kinetic oxygen absorption curves) and is independent of oxygen pressure in the range between 0.5 and 1 atm which Gersmann and Bickel believe[81] to indicate the usual catalytic mechanism involving the formation of a catalyst–substrate complex.

Table 11. Activation energy for the catalysed oxidation of 2,6-di-t-butyl-4-methylphenol in 90% ethanol.[80]

Catalyst	E, cal mole^{-1}
2,6-Di-t-butylbenzoquinone	12000
m-Dinitrobenzene (20 ml/mole)	8900
m-Dinitrobenzene (50 ml/mole)	9400
No catalyst	20000

In the catalysis by quinones the rate of reaction is independent of quinone concentration in the range of the latter investigated and is proportional to oxygen pressure. In the catalytic oxidation of polyphenols such a phenomenon is called saturation of quinone catalysis[83,84]. The independence of the catalytic effect of the concentration of the quinone is due to the formation of a complex[80] between the phenol and the quinone, the interaction with another quinone molecule becoming unlikely.

However, with duroquinone, the catalytic effect does vary with catalyst concentration somewhat. It has been shown[80] that *m*-dinitrobenzene and quinones catalyse the decomposition of *p*-hydroperoxides. Since the decomposition is accompanied by isomerisation, then, on the basis of the data presented, one can probably postulate that the catalytic effect of both nitrobenzenes and quinones is not direct. It is due to the catalytic effect of these compounds on the decomposition of the hydroperoxide.

Since the catalytic effect of *m*-dinitrobenzene on the decomposition of *p*-hydroperoxides is weaker than the effect due to 2,6-di-t-butylbenzoquinone, in the oxidation of phenol higher concentrations of *m*-dinitrobenzene than of the quinone are required for catalysis. It may be supposed that further increase in the amount of catalyst would result in the independence of the reaction rate constant of the concentration of *m*-dinitrobenzene. The possible saturation of the catalytic effect of *m*-dinitrobenzene in the oxidation of trialkylphenols is indicated by the comparison of the activation energies for processes catalysed by different amounts of *m*-dinitrobenzene (Table 11). Table 11 shows that, on going from 20 to 50 ml of *m*-dinitrobenzene per mole, the activation energy is virtually constant, but the rate constant increases almost by a factor of two.

In our experiments the addition of benzoquinone at the beginning of the oxidation with molecular oxygen of 4-aminoalkyl-2,6-di-t-butylphenols in a 1 : 1 alkaline aqueous alcoholic medium leads to an increase of the induction period on the kinetic curve for the consumption of the phenol. The addition of 2,6-di-t-butyl-1,4-benzoquinone at the beginning of the oxidation of 4-aminoethyl-2,6-di-t-butylphenol (XX) does not affect the induction period, but after the induction period the rate of consumption of the phenol (XX) is much lower in experiments with the addition of this quinone than without it. Probably the observed effect is associated with the reduction of the phenoxy-radicals under the influence of the benzoquinone to the initial phenol, while in the presence of 2,6-di-t-butyl-1,4-benzoquinone the phenoxy-radicals are not reduced. The effect of 2,6-di-t-butyl-1,4-benzoquinone begins when a sufficient amount of hydroperoxides accumulates in the system, their decomposition to the initial phenol and the quinone being catalysed by 2,6-di-t-butyl-1,4-benzoquinone. As a result, the *o*-quinone does not accumulate in the system in amounts necessary for an autocatalytic process.

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Stable Phenoxy-radicals

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The present review is devoted to an examination and analysis of published data on reactions leading to the formation of phenoxy-radicals, and the structures and properties of these radicals.
In the description of the methods of preparing phenoxy-radicals, we examine the interaction of sterically hindered phenols with organic peroxides and inorganic oxidising agents, the mechanism of the thermal decomposition of cyclohexadienones, the autoxidation of sterically hindered phenols, and also the action of γ-radiation and ultraviolet radiation on phenols.
In the section devoted to the properties of phenoxy-radicals, we discuss the influence of steric hindrance of the reactive centre, and also the degree of delocalisation of the unpaired electron, on the stability of the phenoxy-radicals.
The available published data on the chemical transformations of substituted phenoxy-radicals are reviewed. Their recombination, disproportionation, isomerisation, and reaction with oxygen and halogens are examined. The influence of the steric and polar properties of substituents on the kinetics and mechanism of the transfer of hydrogen from organic compounds to stable phenoxy-radicals is analysed. The bibliography contains 180 references.

CONTENTS

I. Introduction
II. Reactions leading to the formation of phenoxy-radicals 435
1. Reaction of sterically hindered phenols with peroxo-compounds 435
2. Reaction of sterically hindered phenols with inorganic oxidising agents 436
3. Decomposition of cyclohexadienones 437
4. The autoxidation of sterically hindered phenols 438
5. Action of γ-radiation and ultraviolet radiation on phenols 439
III. The properties of phenoxy-radicals 439
1. Properties of sterically hindered phenols 439
2. Stability of phenoxy-radicals 440
3. Reactions of phenoxy-radicals 441

I. INTRODUCTION

Sterically hindered phenols are now widely used as inhibitors of the thermal-oxidative degradation of polymeric materials, and the oxidation of motor fuels, oils, and edible fats[1-3]. Moreover, as shown by Emanuel' and coworkers[4-6], sterically hindered phenols can be used as physiologically active substances in various areas of biological studies.

The protective action of inhibitors of the phenol type is associated with the removal, from the substrate being oxidised, of the $RO_2^{\cdot}$ and $R^{\cdot}$ radicals responsible for the chain reaction: $RO_2^{\cdot} + PhOH \rightarrow ROOH + PhO^{\cdot}$. As a result of this reaction, the active $RO_2^{\cdot}$ or $R^{\cdot}$ radicals are replaced by the $PhO^{\cdot}$ radicals, which have a low activity and are incapable of maintaining the autoxidation chain reaction.

The retarding action of the inhibitor added to the substance being oxidised depends on[1,3]: (1) the activity of the $PhO^{\cdot}$ radical (the lower the activity of the $PhO^{\cdot}$ radical, the stronger the retarding effect), and (2) the rates of the reactions of the radicals $RO_2^{\cdot}$ and $R^{\cdot}$ with the inhibitor.

The development of a modern theory of the action of inhibitors, which might make it possible to control the selection and application of these inhibitors, is closely related to the development of the chemistry of free radicals and the establishment of the regular features of the dependence of their formation and behaviour on structure. In recent years, significant results have been obtained in this field, but these have not been reviewed to a sufficient extent in the chemical literature.

The present review examines reactions leading to the formation of stable phenoxy-radicals from sterically hindered phenols, and also the structure and behaviour of these radicals.

I. REACTIONS LEADING TO THE FORMATION OF PHENOXY-RADICALS

The chief method for the preparation of phenoxy-radicals is by the interaction of phenols with various organic and inorganic oxidising agents, leading to the removal of a hydrogen atom from the hydroxyl group. Phenoxy-radicals can also be obtained by the action of γ-radiation and ultraviolet radiation on phenols, and also as a result of homolytic bond rupture in various organic molecules. In the present chapter we shall examine reactions leading to the formation of stable phenoxy-radicals from sterically hindered phenols, that is, phenols containing various bulky substituents in the *ortho*-position relative to the hydroxyl group.

1. Reaction of Sterically Hindered Phenols with Peroxo-compounds

The thermal decomposition of organic peroxides in inert solvents is a spontaneous unimolecular reaction which takes place with the formation of free radicals[7,8]:

$$ROOR \rightarrow RO^{\cdot} + RO^{\cdot}$$

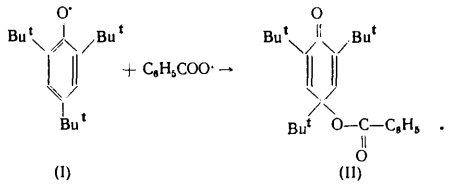
The $RO^{\cdot}$ radicals formed in this reaction can attack phenol molecules, giving the corresponding phenoxy-radicals:

$$PhOH + RO^{\cdot} \rightarrow PhO^{\cdot} + ROH .$$

Phenols react in analogous fashion with the free radicals formed by the decomposition of hydroperoxides, catalysed by cobalt naphthenate[9,10].

The reaction of 2,4,6-tri-t-butylphenol with benzoyl peroxide produces in the solution the blue colour characteristic

of the 2,4,6-tri-t-butylphenoxy-radical (I)[11]. Spectrophotometric study of this process[12] showed that the reaction obeys a second-order kinetic equation and includes as an intermediate stage the formation of the corresponding phenoxy-radical, which subsequently disappears, apparently according to the reaction:



(I) (II)

The direct detection of phenoxy-radicals in the reaction of sterically hindered phenols with peroxo-compounds is now possible using electron paramagnetic resonance (EPR). It was found that the reaction of 2,6-di-t-butyl-4-methylphenol[13,14], 2,6-di-(1,1-dimethylpropyl)-4-methylphenol, 2,6-di-(1,1-dimethylhexyl)-4-methylphenol[13], and 2,4,6-tri-t-butylphenol[14] with benzoyl peroxide, *p*-t-butylcumenyl hydroperoxide, or cyclohexyl peroxocarbonate, leads to the production of EPR spectra which show good agreement with the structures of the corresponding phenoxy-radicals. An interesting feature is that in the work cited no change in the structure of the EPR spectra was observed during the reaction. This indicates that the radicals formed by the decomposition of the peroxides react rapidly with the phenoxy-radicals, and this prevents their further transformation. The nature of the alkyl substituents in the *ortho*- and *para*-positions relative to the phenoxy hydroxyl group influences not only the structure of the final products of the reaction of the phenols with the peroxides, but also its velocity. The study of the dependence of the rate of the reaction of peroxo-radicals with phenols on the structure of the substituents in the phenol molecule is of considerable practical as well as purely theoretical interest, since the retarding action of inhibitors is to a large extent determined by the rate of the reaction of the peroxo-radicals with the inhibitor molecules (the efficiency of the inhibitor); when various inhibitors are introduced into a reaction in equal concentrations, the most effective inhibitor is that which reacts most rapidly.

Ingold[15], in a study of the oxidation of mineral oil in the presence of a number of 2,6-di-t-butyl-4-substituted phenols, found that electron-donating substituents in the *para*-position of the phenol, if their volume is small, increase the relative activity of the inhibitor. A linear relationship is observed between $\lg(k/k_0)$ (where k and k_0 are the rate constants of the inhibitor being studied and a standard inhibitor for the given reaction) and the Hammett constants σ of the substituents. A similar good correlation between the inhibiting activity of 2,6-di-t-butyl-4-alkylphenols and the Hammett constants σ was observed for the oxidation of methyl oleate[16]. With bulky substituents in the *para*-position, the relative inhibiting activities show a good correlation with the Taft constants of the substituents[15], which make allowance for steric factors. Study of the reaction of t-butoxy-radicals with 2,6-di-t-butyl-4-methylphenol† and 2,6-di-t-butylphenol, both deuteriated in the OH group, and also the reaction of styrylperoxo-radicals with 4-alkylphenols, revealed kinetic isotopic effects ($k_H/k_D = 6.14$[17] and $k_H/k_D = 10.5$[18] respectively), indicating that the stage limiting the rate of the process is the transfer of hydrogen from the phenol molecules to the attacking radical. To investigate the influence of substituents on the ease of formation of the polar transition state in the reaction of styrylperoxo-radicals with *meta*-, *para*-,[18] and *ortho*-substituted phenols[19], and also in the reaction of the t-butoxy-radical with 2,4,6-trialkylphenols[20], a correlation was established between the logarithms of the rate constants and the Brown constants σ^+ for electrophilic substituents. A linear relationship was observed with values of the constants for the reaction ρ equal to 1.30 for 2,6-dimethylphenol and 1.11 for 2,6-di-t-butylphenol. The small value of ρ for these phenols indicates only slight separation of the charges in the transition state of this reaction.

Like the RO· and ROO· radicals, hydroxyl radicals react with phenols with the formation of peroxo-compounds of the type PhO–OPh and PhO–OH.[21,22] The system $H_2O_2 + FeSO_4$ (Fenton's reagent) is usually employed as source of ·OH radicals. The formation of phenoxy-radicals in the reaction of 2,6-di-t-butyl-4-methylphenol with hydroxyl radicals was observed by Ershov and Zlobina[23] using the EPR method. The source of hydroxyl radicals used in this instance was peroxonitrous acid, which undergoes homolytic splitting in solution with the formation of ·OH and $\cdot ONO \rightleftharpoons \cdot NO_2$ radicals[24,25]. Analogous results were obtained by Ershov and coworkers[26] using alkyl nitrites as oxidising agents; these compounds readily undergo homolytic splitting with the formation of RO· and NO· radicals. The decomposition of alkyl nitrites in the presence of alkylphenols leads to the production of the corresponding phenoxy-radicals, detected both from the appearance of the characteristic colour and from the EPR spectra.

2. Reaction of Sterically Hindered Phenols with Inorganic Oxidising Agents

The reactions of sterically hindered phenols with peroxo-compounds, described above, generally produce, in addition to the primary phenoxy-radical, various products of the addition of the peroxide residue to this radical. In order to study the stability and behaviour of phenoxy-radicals it is necessary to carry out the oxidation of the phenols in such a way that the substrate containing the PhO· radicals does not contain other active radicals capable of recombining with the PhO· radicals. These requirements are satisfied by such oxidising agents as lead dioxide[12,14,27-33,35-37], silver oxide, potassium hexacyanoferrate(III)[38-42], and cerium(IV) sulphate[43,44]. The oxidation of phenols by these oxidising agents can be represented in general form as follows:

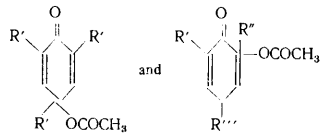
$$PhOH + M^{n+} \rightarrow PhO^{\cdot} + M^{(n-1)+} + H^+.$$

Using these oxidising agents, it has been established that the phenoxy radicals formed by the oxidation of phenols have different stabilities, and this determines their ability to undergo further transformations. Thus the oxidation of 2,4,6-tri-t-butylphenol[28,45-48] and various other phenols leads to the formation of phenoxy-radicals which are able to "live" in the absence of oxygen for a very prolonged period. On the other hand, the oxidation of 2,6-di-t-butyl-4-methylphenol produces a less stable phenoxy-radical, transformation of which gives various final products. Phenols which do not contain bulky substituents in the *ortho*-position are oxidised with the formation of even less stable radicals, whose lifetimes decrease to hundredths of a second. In order to study these radicals by the EPR method, it is necessary to establish a steady-state concentration of the radicals sufficient for their detection. Parti-

† In the Russian text here and subsequently this compound is incorrectly referred to as Ionol [which is 2-(3-hydroxybutenyl)-1,3,3-trimethylcyclohexene]. This has been corrected in the translation (Ed. of Translation).

cularly fruitful results have been obtained using a flow system in which the solutions of the phenol and the oxidising agent are mixed directly in the resonator of the EPR spectrometer. Stone and Waters[43,44] used this method to study the EPR spectra and structure of the radicals formed in the oxidation of a number of unhindered or weakly hindered phenols. In some instances, when the oxidation of the phenols takes place too rapidly, a milder oxidising agent—mercuric oxide HgO—is used[37]. The formation of phenoxy-radicals in the oxidation of 2,6-di-t-butyl-4-methylphenol by HgO is observed only when the solution is heated to 60°C,[50] whereas oxidation by means of PbO_2 or $K_3Fe(CN)_6$ leads to the immediate production of phenoxy-radicals even at room temperature[50-53].

The oxidation of phenols by lead tetra-acetate [$Pb(CH_3COO)_4$] and acetyl peroxide leads to the formation of the corresponding *p*- and *o*-quinol acetates[54-58]:



where R′ = CH_3, R″ = CH_3 or H, and R‴ = CH_3.

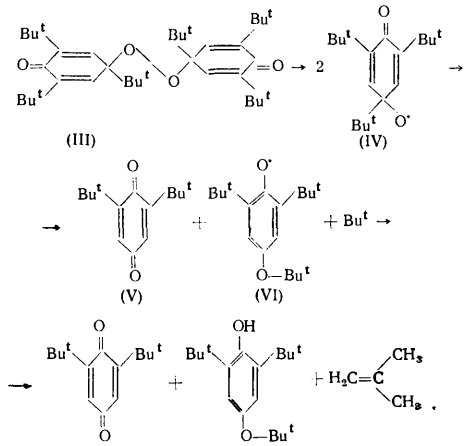
The radical mechanism of the reaction of phenols with $Pb(CH_3COO)_4$ was proved by Emanuel' and coworkers[59] by the production, in the EPR spectra, of signals due to primary phenoxy radicals from 2,4,6-tri-t-butylphenol, 2,6-di-t-butylphenol, and 2,6-di-t-butyl-4-ethylphenol. These workers also noted the formation of radicals from unhindered phenols such as *p*-cresol, *p*-ethylphenol, and phenol, confirming that this reaction also takes place by a radical mechanism with unhindered phenols. The formation of radicals from unhindered phenols in this instance is rather surprising, since when other oxidising agents were used, these radicals could not be recorded, because of their extremely low stability. It may be suggested that the short-lived radicals produced in the oxidation of phenols by lead tetra-acetate may form a complex with the oxidising agent or with its decomposition products, leading to their stabilisation.

The oxidation of sterically hindered phenols by salts of carboxylic acids, for example $Cu(OCOR)_2$, probably also takes place by a radical mechanism, since the chief reaction products, as in the reactions of such one-electron oxidising agents as PbO_2 and $K_3Fe(CN)_6$, are dimers, which are paired in the *ortho*- and *para*-positions, depending on the structure of the original phenol[60].

Phenoxy-radicals were observed directly by the EPR method by Razuvaev and coworkers[61,62] in a study of the oxidation of phenols in the presence of a complex Cu^{2+} + amine catalyst.

3. Decomposition of Cyclohexadienones

As already noted, the homolytic mechanism of the decomposition of organic peroxides of the type ROOR is now generally accepted[36]. The production of radicals in their decomposition has been confirmed by various methods, in particular from the initiation of autoxidation and polymerisation in the presence of the decomposing peroxide, from the decrease in the rate of decomposition of the peroxide in the presence of inhibitors of free-radical reactions, etc. Until recently, however, it was not possible to observe free radicals directly in the thermal decomposition of organic peroxides, since these radicals are insufficiently stable for detection by the EPR method. Brodskii and Pokhodenko[63] tried to prove the homolytic mechanism of the decomposition of peroxides using the EPR method. They started from the assumption that if the RO residues in the molecule of the peroxide ROOR were stable phenoxy-radicals, the decomposition by a homolytic mechanism would give radicals sufficiently stable to be recorded by the EPR method. For this purpose, bis-(1,3,5-tri-t-butyl-4-oxocyclohexa-2,5-dienyl) peroxide (III) was synthesised[27,28,46,64]. It was previously found[28,65] that the products of the decomposition of this peroxide are 2,6-di-t-butyl-4-t-butoxyphenol, 2,6-di-t-butylbenzoquinone, and 2-methylpropene. To explain the formation of these products, Muller[65] suggested that the decomposition of the peroxide takes place by an ionic mechanism with transfer of the t-butyl residue from the carbon atom to the oxygen atom. When this peroxide was heated to 200°C, however, an intense EPR signal was observed[63], consisting of three components 1 : 2 : 1 with a splitting between them equal to 1.3 Oe. The infrared spectra of the decomposition products of the peroxide[63], unlike the spectrum of the original peroxide, showed a band at 3650 cm^{-1}, corresponding to the OH group of sterically hindered phenols. On this basis, the following mechanism was proposed for the decomposition of the peroxide (III); this mechanism explains the production of the final products:

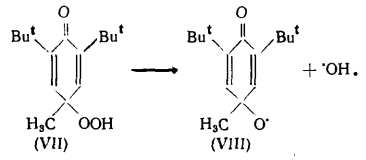


The observed EPR spectrum of the decomposition products of the peroxide is due to the phenoxy-radical (VI), in which the unpaired electron interacts with two equivalent *m*-hydrogen atoms. The constant for the splitting between the components of this signal has a value which is close to that previously obtained[53] for this radical, formed by the oxidation of the corresponding phenol. The suggestion[66,67] that the triplet EPR signal observed in the decomposition of the peroxide is due to the radical (IV), in which the presence of the oxygen atom in the *para*-position leads to a decrease in the splitting constant, which is usually equal to 1.7 Oe for the 2,4,6-tri-t-butylphenoxy-radical, to 1.3 Oe, appears erroneous if allowance is made for the low probability of the observation of this radical in the EPR spectra, resulting from its low stability, which is due to the impossibility of delocalisation of the unpaired electron in the benzene ring and the absence of bulky groups screening the reactive centre.

The radical mechanism for the decomposition of the peroxide (III) was later proved by the EPR method by carrying out the reaction in xylene solution at 80°C.[68]

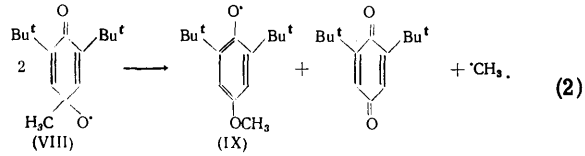
The thermal decomposition of 2,6-di-t-butyl-4-hydroperoxy-4-methylcyclohexa-2,5-dienone (VII) is also accompanied by the formation of phenoxy-radicals[69]. On the

basis of generally accepted ideas, this process should be represented as follows:



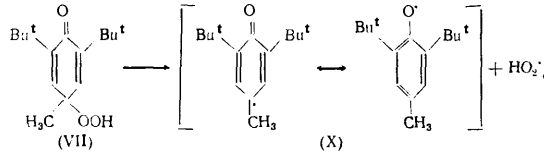
(VII) (VIII) (I)

Subsequent disproportionation of the radicals (VIII) should produce the phenoxy-radical (IX), as described above:



(VIII) (IX) (2)

The EPR signal observed in this work (1 : 3 : 3 : 1 quadruplet, 1 : 2 : 1 triplet, a_1 = 11 Oe, and a_2 = 1.7 Oe), however, cannot be attributed either to radical (VIII) or to radical (IX), formed according to schemes (1) and (2). The parameters of this spectrum (the number of lines, the ratio of the intensities, and the splitting constants) correspond completely to the 2,6-di-t-butyl-4-methylphenoxy-radical (X)[51,52,66]. On this basis it was suggested[69] that the first stage in the decomposition of the hydroperoxide is the removal of the hydroperoxo-radical with the formation of a phenoxy-radical:



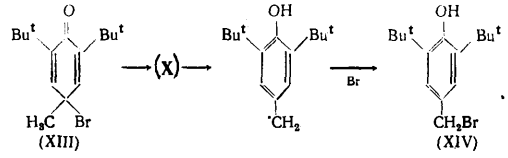
(VII) (X)

This unusual course of the thermal decomposition of organic peroxo-compounds without rupture of O–O bonds was also observed by the action of heat on 2,6-di-t-butyl-4-t-butylperoxy-4-methylcyclohexa-2,5-dienone (XI), leading to the formation of 2,6-di-t-butyl-4-methylphenoxy-radicals[70], and on bis-(3,5-di-t-butyl-4-oxo-1-phenyl-cyclohexa-2,5-dienyl) peroxide (XII), accompanied by the formation of 2,6-di-t-butyl-4-phenylphenoxy-radicals[71].

The radicals formed by the thermal decomposition of organic peroxides are effective initiators of polymerisation processes[7,8]. The thermal decomposition of the peroxide (III)[50], which, as indicated above, takes place with rupture of the O–O peroxide bond, gives radicals which initiate the polymerisation of methyl methacrylate. On the other hand, the decomposition of the hydroperoxide (VII) in the presence of methyl methacrylate and vinyl acetate does not lead to polymerisation of the latter[69], in agreement with the earlier observation[71] that the polymerisation of acrylonitrile is not initiated by the decomposition products of the peroxide (XII), whose decomposition also takes place without rupture of the peroxide bond.

It can be seen from the foregoing that the peroxo-compounds formed from sterically hindered phenols may decompose in two ways when heated: with splitting of the peroxide bond [peroxide (III)] or with splitting of the C–O bond of the C–O–O–R group [peroxides (VII), (XI), and (XII)]. In this instance, when splitting takes place at the O–O bond, active radicals of type (IV), which initiate the polymerisation of monomers, are produced. On the other hand, the phenoxy and peroxo-radicals produced in the decomposition of peroxides with rupture of the C–O bond of the C–O–O–R group do not initiate the polymerisation of monomers, because of their comparatively high stability.

One example of the decomposition of cyclohexadienone structures with the formation of phenoxy-radicals is the quinonone-benzyl rearrangement of 2,6-di-t-butyl(-4-methylphenol quinobromide (XIII)[72], which reacts when heated to give the corresponding hydroxybenzyl bromide (XIV). The available published data could be used to ascribe to this process either an ionic mechanism[73] or a radical mechanism[74]. According to recent results[72], thermal treatment of (XIII) in the resonator of an EPR spectrometer leads to the production of an EPR signal corresponding to the 2,6-di-t-butyl-4-methylphenoxy-radical (X)[51,52]. On this basis, the following reaction scheme was suggested[72]:



(XIII) (XIV)

The phenoxy-radical (X) is also formed when (XIII) is treated with benzoyl peroxide, metallic mercury, or ultraviolet light. The formation of the corresponding phenoxy-radical has also been recorded by similar treatment of the quino-bromide of 2,4,6-tri-t-butylphenol[72].

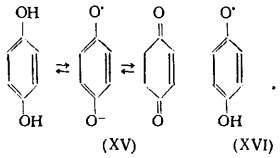
4. The Autoxidation of Sterically Hindered Phenols

The autoxidation of organic compounds is accompanied by the formation of free radicals[1,3] which in a number of instances are recorded by the EPR method[66].

In the oxidation of sterically hindered phenols, the formation, as final products, of compounds of the type PhO–OH and PhO–OPh[75–80], analogous to the products of the radical reaction of sterically hindered phenols with organic peroxides (see part 1 of this section), has been observed. The radical mechanism of the autoxidation of phenols was recently confirmed experimentally by the EPR method.

Adams and coworkers[81] observed the production of eight lines (1 : 1 : 3 : 3 : 3 : 3 : 1 : 1) in the EPR spectrum during the autoxidation of 2,6-di-t-butyl-4-methylphenol in alkaline medium. No explanation was put forward in the work cited for this structure of the EPR spectrum. Autoxidation was later studied in more detail[82] for the example of a number of 2,6-di-t-butyl-4-R-phenols. It was shown that the reaction leads to the formation of radical-ions of the semiquinone of the substituted pyrocatechol, recorded by the EPR method.

The autoxidation of *p*-hydroxyphenols (hydroquinones) is also accompanied by the formation of semiquinone radical-ions; this was proved as early as the nineteen-thirties by Michaelis and coworkers[83,84]:



(XV) (XVI)

The radical-ion formed in this reaction is stabilised by resonance, so that it can be observed by the EPR method. The EPR spectrum of (XV)[85,86], consisting of a quintuplet 1 : 4 : 6 : 4 : 1 (a = 2.37 Oe), is in agreement with the equivalence of all four protons of the benzene ring.

The semiquinone radical-ion has proved to be a convenient object for the study of the influence of substituents on the distribution of spin density in the ring[87], for the investigation of the inductive effect of substituents[88,89], and for the experimental verification of the theory of hyperconjugation[90].

Unlike (XV), the undissociated semiquinone (XVI) has a low stability and it has not been detected by the direct method.

Recently, Pokhodenko and Khiznhyi[91] detected uncharged semiquinone radicals in neutral medium (benzene) by the EPR method during the oxidation of hydroquinones containing bulky alkyl substituents in the *ortho*-positions. Thus in the oxidation of a solution of 2,6-di-t-butylhydroquinone in benzene with PbO_2, a triplet signal (1 : 2 : 1) is produced with splitting constant 1.75 Oe, corresponding to the uncharged semiquinone radical. The autoxidation of this compound in alkaline medium also gives a triplet signal, but with a reduced hyperfine splitting constant (1.2 Oe), assigned to the semiquinone radical-ion. The stabilities of the uncharged and charged semiquinone radicals differ considerably from one another: removal of the oxidising agent (PbO_2) in the first instance leads to the immediate disappearance of the EPR signal, whereas thorough evacuation of the oxidising agent (oxygen) in the second instance does not lead to rapid disappearance of the EPR signal.

5. Action of γ-Radiation and Ultraviolet Radiation on Phenols

It can be seen from the foregoing that most reactions leading to the formation of phenoxy-radicals are associated with the removal of hydrogen from the hydroxyl group of the phenol under the influence of oxidising agents. In recent years it has been shown that the rupture of the O–H bond in phenols with the formation of radicals may be brought about under the influence of ionising radiation. Thus the action of X-rays or ultraviolet light on 2,4,6-tri-t-butylphenol in the solid state or in benzene solution leads to the formation of a stable radical, whose EPR spectrum consists of a single line with a breadth of 3 Oe[92]. The irradiation of 2,4,6-tri-isopropylthiophenol leads to the formation of the corresponding disulphide[92], but the EPR spectrum could not be recorded, apparently due to the low stability of the radical produced. The detection of unstable radicals on irradiation is facilitated by the use of low temperatures. Thus the EPR spectra of radicals obtained by the photolysis of a number of thiophenols at 77°K [93] or by the γ-irradiation of solid bis-phenol[94] have been studied. The EPR method has been used to detect the formation of primary phenoxy-radicals when ultraviolet radiation is used for the initiation of the decomposition of t-butyl peroxide in the presence of a number of phenols at temperatures reaching −30°C.[95]

III. THE PROPERTIES OF PHENOXY-RADICALS

1. Properties of Sterically Hindered Phenols

Sterically hindered phenols, whose oxidation produces phenoxy-radicals, exhibit a number of specific properties. The presence of screening alkyl substituents in the *ortho*-positions relative to the hydroxyl group of the phenol leads to the loss of such typical properties of phenols as solubility in water and alkalis, the ability to give colour reactions with $FeCl_3$, and the ability to react with metallic Na, RMgBr, or diazomethane[96,97].

Bulky *ortho*-substituents hinder the reaction of the hydrogen of the O–H group with other molecules, and this influences reaction rates and the ability to form a hydrogen bond. The retarding action of bulky substituents on the rate of the reaction of phenols with peroxides was noted earlier. Thus in a study of the reaction of $RO_2^{\cdot}$ radicals with 2,6-dialkyl-4-methylphenols it was found that the rate of the process decreases with increase in the volume of the substituents in positions 2 and 6, in the following order: 2,6-dimethyl > 2,6-di-isopropyl > 2-t-pentyl > 2-t-octyl > > 2,6-di-t-butyl > 2,6-di-t-pentyl > 2,6-di-t-octyl > > 2-t-butyl-6-t-octyl[19,20]. An analogous influence of substituents was also noted in studies of the rates of the oxidation of phenols by lead tetra-acetate[55] and the acetylation[98] and alkylation of alkyl halides[99].

Steric hindering of the hydroxyl group of the phenol leads to a sharp decrease in its acidity, as with carboxylic acids[100–102]. Large groups hinder the solvation of the anion formed as a result of the dissociation, and hence decrease its stability. Moreover, it is possible that alkyl substituents in the phenol molecule, as in hindered acetic acids, decrease the effective dielectric constant around the OH group, increasing the electrostatic energy of the anion and hence decreasing the dissociation constant[100,101].

It is natural to assume that the steric hindering of the hydroxyl group is also responsible for the decrease in the electrical conductivity of solutions of substituted phenols. The ratio of the conductivities of the *p*-alkylphenol and its *o*-isomer in solution is equal to 14 for the cresols, 336 for the isopropylphenols, and 136 for the t-butylphenols[103].

As already noted, the hindering of the hydroxyl group by bulky substituents in the *ortho*-positions prevents the formation of associates of the substituted phenols with other molecules. A large number of studies have shown that unlike unsubstituted phenol[104–106], sterically hindered phenols show no tendency to form intermolecular hydrogen bonds[107–110]. For 2,6-di-t-butyl-4-methylphenol, the appearance in the infrared spectra of weak bands corresponding to hydrogen bonds is observed only in strongly basic solvents[111]. Groups which are less bulky than t-butyl have a smaller influence on hydrogen bond formation[109,112,113].

The study of phenol solutions by nuclear magnetic resonance (NMR) also confirms that steric factors have a decisive influence on the possibility of hydrogen bond formation[114–117]; a good correlation is observed between the magnitude of the chemical shift resulting from hydrogen bonding[117] and the displacement of the frequencies in the infrared spectra[107].

The frequencies of the stretching vibrations of the hydroxyl group in phenol are altered by the introduction of alkyl substituents in the *ortho*-positions, and the increase in frequency for 2,6-di-t-alkylphenols relative to unsubstituted phenol ($\Delta\nu = 34$ cm^{-1})[118–120] is too large to be attributed entirely to the inductive influence of the alkyl substituents.

At first sight, this increase in the frequency of the stretching vibrations of the hydroxyl group can be attributed to the breakdown of the coplanarity of the OH group and the ring, since this would lead to a decrease in conjugation and an increase in frequency. Proof of this influence of substituents on the coplanarity of individual groups of molecules has been published[121–124]. Study of the frequencies of the stretching vibrations of the OH group in 4-substituted

and 2,6-dialkyl-4-substituted phenols shows, however, that the frequencies and intensities of the bands show a good correlation with the Hammett constants σ of the substituents[108,118-120]. The slope of the straight lines is the same in both instances[118] and is equal to 13.7 cm^{-1}. On this basis it was concluded that the OH group in 2,6-dialkylphenols, as in phenols which have no substituents in the *ortho*-positions, is coplanar with the ring. Ingold[120] attributed the observed increase in frequency to the interaction of the electron clouds of the hydroxyl and *ortho*-alkyl groups. A similar explanation was used to interpret the results of a study of the chemical shifts of the NMR signal from the OH group of a number of mono- and di-ortho-substituted phenols, which showed that the screening of the hydroxyl proton increases with increase in the volume of the *ortho*-substituent[125]. Comparison of the values of ν and τ shows a correlation between these quantities, apparently indicating that the same factors are responsible for the change in these quantities. Although these results confirm the coplanarity of the OH group and the ring, the accuracy of the experiments does not exclude the possibility that there is slight rotation. The energy of conjugation of this group with the ring changes as $\cos^2\theta$ (where θ is the angle of rotation)[121,126], that is, even a fairly marked rotation of the bond under the influence of bulky substituents does not eliminate the conjugation completely. Thus for small values of θ this difference in the infrared spectra may not be detected.

The facts examined in this section indicate the highly specific nature of sterically hindered phenols, resulting from the presence of bulky alkyl substituents in the *ortho*-positions relative to the hydroxyl groups. The steric screening is also responsible for a number of the unusual properties of the radicals formed by the removal of hydrogen from the hydroxyl group of these phenols, particularly their high stability.

2. Stability of Phenoxy-radicals

The factors leading to the stabilisation of radicals have been examined in most detail for the example of the triphenylmethyl radicals formed by the dissociation of hexaphenylethane[7,127-129]:

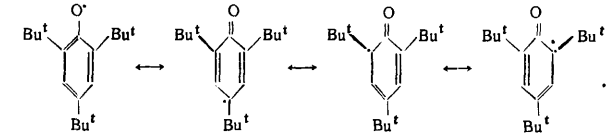
$$(C_6H_5)_3C{-}C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C^{\cdot}.$$

The chief factors determining the stability of free radicals are: (1) the extent of the steric hindrance of the atom formally carrying the unpaired electron; and (2) the extent of the delocalisation of the unpaired electron.

The introduction of phenyl groups into the *para*-positions of the benzene rings of the triphenylmethyl radical leads to an increase in the stability of the radical[130,131], due to the additional possibilities for delocalisation of the unpaired electron[132]. An analogous influence is observed when the phenyl rings are replaced by naphthyl rings. On the other hand, substituents in the *ortho*-positions of the phenyl rings lead to greater stabilisation of the radical than the same substituents in the *para*-position[133,134]. In the opinion of Razuvaev and coworkers[135], the stability of the radical may be due to intramolecular and intermolecular stabilisation. Study of the kinetics of the disappearance of substituted naphthoxy-radicals has shown the importance of both steric and energetic factors. Increase in the stability of radicals also takes place as a result of the formation of complexes with electron-donating solvents. The possibility of interaction between free radicals and the medium was also proved[137] by the EPR method for the example of nitrogen oxide radicals, which form a hydrogen bond with the participation of the unpaired electron with polar solvents.

Let us now consider the factors leading to the stabilisation of phenoxy-radicals.

The infrared spectra and EPR spectra‡ have shown that sterically hindered phenoxy-radicals are characterised by delocalisation of the unpaired electron[138]:



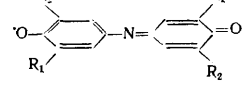
The infrared spectra of phenoxy-radicals shows a doublet band in the range 1600–1660 cm^{-1}. The presence of this band, which is characteristic of the C–O bond in 2,5-cyclodienones and substituted diphenoquinones[80,142-146], indicates that there is a marked contribution from the quinonoid structure in the overall state of the radical. This delocalisation of the unpaired electron leads to an increase in the stability of the phenoxy-radical.

When the t-butyl group in the *para*-position of the radical is replaced by a methoxy- or t-butoxy-group, the stability of the radical remains unchanged. This is apparently due to the participation of the ether oxygen in the overall conjugation, and this stabilises the radical to a sufficient extent, although the ether group in the *para*-position occupies less space than the t-butyl group[138].

The most important factor responsible for the stabilisation of phenoxy-radicals, however, is the steric hindering of the phenoxy-oxygen by bulky alkyl substituents. Thus the 2,4,6-tri-t-butylphenoxy-radical in the absence of oxygen may exist for as long a period as desired, whereas the 2,4,6-trimethylphenoxy-radical has a low stability and undergoes various changes. As already noted, the replacement of a t-butyl group in the *para*-position by the t-butoxy-group does not alter the stability of the radical. On the other hand, the replacement of an *ortho*-t-butyl group by an *ortho*-t-butoxy-group leads to a sharp decrease in stability. The gain in conjugation energy obtained due to the ether oxygen is insufficient to stabilise the sterically less hindered radical.

In recent years a number of attempts have been made to study the stability of phenoxy-radicals quantitatively. Thus Cook and coworkers[33] studied the disappearance of 2,6-di-t-butyl-4-isopropylphenoxy-, 2,6-di-t-butyl-4-cyclohexylphenoxy-, and 4-s-butyl-2,6-di-t-butylphenoxy-radicals from the change in the optical density of their solutions at 630 nm. The kinetic results obtained show that the rate of disappearance of these radicals decreases in the following order of substituents in the 4-position of the phenol: isopropyl > cyclohexyl > s-butyl. The rates of disappearance of the 2,6-di-t-butyl-4-methylphenoxy- and 2,6-di-t-butyl-4-ethylphenoxy-radicals was found to be so great that it could not be measured by the spectrophotometric method.

Extensive possibilities for the study of the stability of free radicals are provided by the EPR method. By using this method, it has been possible to determine the influence of the degree of steric hindrance of the phenoxy-oxygen of a number of indophenoxy-radicals on their stability[147]:



$R_1 = R_2 = t\text{-}C_4H_9$, (XVII)
$R_1 = R_2 = t\text{-}C_5H_{11}$, (XVIII)
$R_1 = R_2 = \text{cyclo-}C_6H_{11}$, (XIX)
$R_1 = R_2 = \text{iso-}C_3H_7$, (XX)
$R_1 = t\text{-}C_4H_9$; $R_2 = CH_3$. (XXI)

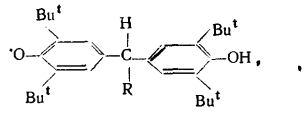
‡ The EPR spectra of a large number of phenoxy-radicals have now been studied[52,53,66,181].

It was shown that the radicals (XVII) and (XVIII), which do not contain α-hydrogen atoms in the *ortho*-substituents, have an extremely high stability; their concentrations in benzene or xylene solutions do not change to a significant extent as far as 70°C. On the other hand, the radicals (XIX), (XX), and (XXI), which contain α-hydrogen atoms in the *ortho*-substituents, have a much lower stability.

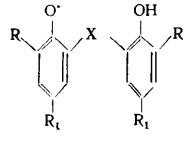
Comparison of the rate constants for the disappearance of the three indophenoxy-radicals (XIX), (XX), and (XXI) showed that their stability depends to a marked extent on the structure of the *ortho*-substituents. The ratio of the rate constants for the disappearance of the radicals studied is approximately

$$K_{XIX} : K_{XX} : K_{XXI} = 1 : 2 : 50.$$

The sharp increase in the rate of disappearance on going from the radicals (XIX) and (XX) to the radical (XXI) is due to the increase, by four orders of magnitude, in the value of the pre-exponential term, indicating that the *ortho*-substituents have a much smaller hindering effect on the reactive centre in radical (XXI) than in the radicals (XIX) and (XX). It is of interest to compare the stability of the radicals formed by the oxidation of *p*- and *o*-bis-phenols[148]. In the study of the oxidation of *p*-bis-phenols by the EPR method:



where R = H or C_6H_5, it was found that the phenoxy-radicals formed in the reaction have a high stability (for the radical with R = C_6H_5, $\tau_{1/2}^{40^\circ}$ = 1050 s). This is due to the extremely low value of the pre-exponential term ($K_0 = 3.2 \times 10^3\ s^{-1}$, $\Delta S^{\neq} = 60$ e.u.), and this in turn is due to the marked restrictions in the elementary stage of the disappearance of the phenoxy-radical. On the other hand, the phenoxy-radicals formed in the oxidation of *o*-bis-phenols have such a low stability that the authors cited[148] could not determine it quantitatively by the EPR method



X = CH_2, CH-C_6H_5, -S-;
R = t-C_4H_9, $C(CH_3)_2C_6H_5$;
R_1 = CH_3, C_2H_5, t-C_4H_9.

The reason for such a sharp decrease in stability on going from the *p*- to the *o*-bis-phenoxy-radicals is apparently the marked decrease in the steric hindering of the phenoxy oxygen by the ortho-substituents. In the *p*-bis-phenoxy-radicals studied, the oxygen is surrounded by bulky *o*-t-butyl groups, whereas in the *o*-bis-phenoxy-radicals one of the *ortho*-positions relative to oxygen is occupied by $-CH_2-$ or $-CH-C_6H_5$-groups or sulphur atoms, which have a smaller hindering effect than the *o*-t-butyl groups. Decrease in the degree of hindrance of the phenoxy-oxygen by *ortho*-substituents, as shown above for substituted indophenoxy-radicals, leads to a sharp decrease in the stability of the resulting radical.

The stability of phenoxy-radicals is also influenced to a significant extent by the degree of branching of the carbon atom of the alkyl substituent in the *para*-position.

Comparison of the rate constants of the disappearance and the transformation half-periods for 2,6-di-t-butyl-4-R-phenoxy-radicals (R = CH_3, C_2H_5,[149] or t-C_3H_7 [33]) indicates that their stability increases in the order of *para*-substituents: $CH_3 < C_2H_5 <$ iso-$C_3H_7 <$ t-C_4H_9.

An interesting feature is that the stability of the radicals formed by the oxidation of 2,6-di-t-butyl-4-alkylphenols is much less than that of the *p*-bis-phenoxy-radicals, due to the additional possibilities for delocalisation of the unpaired electron in the second instance. The 2,4,6-tri-t-butyl-phenoxy-radical, which does not contain α-hydrogen atoms in the *para*-substituent, is exceptionally stable and may exist for a prolonged period in the absence of oxygen.

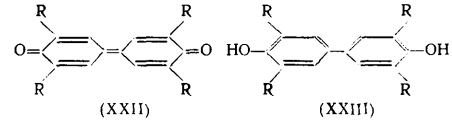
The examples considered in this section show that, as with the triphenylmethyl radicals, the chief factors responsible for the stability of phenoxy-radicals are the delocalisation of the unpaired electron and the extensive steric hindrance of the atom carrying a large proportion of the charge of the unpaired electron. These two effects explain the characteristic behaviour of phenoxy-radicals in chemical reactions. Let us consider some of these reactions.

3. Reactions of Phenoxy-radicals

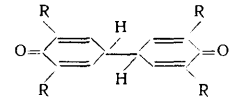
a. Recombination. As already noted, the phenoxy-radicals formed by the oxidation of 2,4,6-trialkylphenols which do not contain labile α-hydrogen atoms in their substituents are generally stable and do not undergo significant changes in the absence of oxygen. The recombination of these radicals is prevented by bulky substituents in the *ortho*- and *para*-positions. On the other hand, 2,6-di-t-alkylphenoxy-radicals with substituents in the *para*-position capable of conjugation with the unpaired electron exist in equilibrium with their dimers[53,150]. This dimer exists, for example, for the 2,6-di-t-butyl-4-cyanophenoxy-radical, whose unpaired electron is capable of conjugation with the substituent and can be found on the nitrogen atom.

The existence of a dimer has also been demonstrated[151] for the 2,4,6-triphenylphenoxy-radical, but its structure has not been determined[136,152].

The oxidation of 2,6-dialkylphenols containing a hydrogen atom in the *para*-position is accompanied by the formation of phenoxy-radicals and produces dimeric final products. Thus in the oxidation of 2,6-dimethylphenol or 6-t-butyl-2-methoxyphenol by lead dioxide[64], potassium hexacyanoferrate(III) in an alkaline medium[141,153,154,156], organic peroxides[21,22,79,157], and oxygen[62], the chief products of the reaction are the diphenoquinone (XXII) and its dihydroxy-derivative (XXIII), whose structures were confirmed from the infrared and ultraviolet spectra:



(XXII) (XXIII)



(XXIV)

The intermediate product (XXIV) is comparatively stable only in non-polar solvents and undergoes rapid isomerisation to the corresponding dihydro-derivative in polar media[64,141].

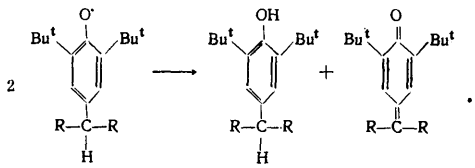
Analogous dimeric products are also formed in the oxidation of 2,6-di-t-butyl-4-chloro(bromo)phenols[36].

Study of the oxidation of phenols in which one or both *ortho*-positions were unsubstituted[21,22,60,62,71,154-156] showed that dimers joined in the *ortho*-positions are formed. These reactions involving the recombination of phenoxy-radicals show the importance of the influence of steric factors on the direction of the process. In all instances,

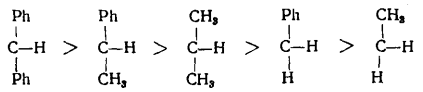
recombination takes place at the least screened position of the radical, carrying the unpaired electron.

b. Disproportionation of phenoxy-radicals. The introduction of secondary alkyl substituents into the *para*-position of 2,6-di-t-butylphenols leads to a decrease in the stability of the corresponding radicals relative to radicals whose *para*-position is occupied by tertiary alkyl substituents.

In a study of the disappearance of the blue 2,6-di-t-butyl-4-isopropylphenoxy- and 4-s-butyl-2,6-di-t-butylphenoxy-radicals, it was found that they are converted not into dimeric products but into the corresponding yellow quinone methides. Spectrophotometric study of the kinetics of this reaction showed that the rate of disappearance is described by an equation of second order with respect to the radical. On this basis, the following reaction scheme was proposed:



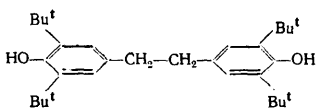
The formation of quinone methides and the original phenols was also observed in a study of the disappearance of a number of other phenoxy-radicals[158,159]. Study of the rate of disappearance of phenoxy-radicals by disproportionation has made it possible to estimate qualitatively the influence of a substituent in the *para*-position on the stability of the radicals[158,159]. It was found that the stabilities of the phenoxy-radicals decrease in the following order of substituents:



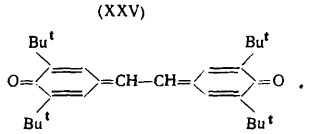
Examination of this series of substituents confirms the stabilising influence of the phenyl group on the radical.

c. Isomerisation of phenoxy-radicals. When the number of α-hydrogen atoms in the *para*-substituent of a 2,6-di-t-butylphenol is increased, the products of the oxidation of these phenols differ from those obtained from *p*-s-alkylphenols.

Thus the chief products of the oxidation of 2,6-di-t-butyl-4-methylphenol are 4,4′-ethylenebis-(2,6-di-t-butylphenol) (XXV) and 4,4′-ethanediylidenebis-(2,6-di-t-butylcyclohexa-2,5-dien-1-one) (XXVI):



(XXV)

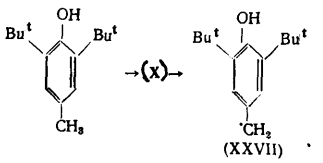


(XXVI)

The formation of these products led a number of authors[27,79,80] to suggest that the primary act in the oxidation of 2,6-di-t-butyl-4-methylphenol involves the removal of a hydrogen atom of the methyl group with the formation of the hydroxybenzyl radical (XXVII), whose dimerisation produces (XXV). Subsequent oxidation of (XXV) gives the final stilbenequinone (XXVI).

On the other hand, the formation of cyclohexadienone structures in the oxidation of 2,6-di-t-butyl-4-methylphenol by organic peroxides suggests the existence of phenoxy-radicals, whose presence in 2,6-di-t-butyl-methylphenol undergoing oxidation was later established reliably by spectroscopic methods, including the EPR method[51-52,141]. The formation of phenoxy-radicals as primary products of the oxidation of 2,6-di-t-butyl-4-methylphenol made it difficult to explain the production of the dimers (XXV) and (XXVI), since direct conversion into these compounds from the phenoxy-radical is impossible.

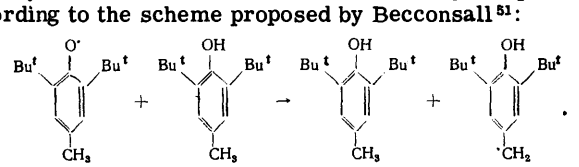
To resolve these contradictions, Cook[29] suggested that the initially formed phenoxy-radical (X) subsequently undergoes isomerisation to form the hydroxybenzyl radical, according to the scheme:



(XXVII)

The radical (XXVII) then undergoes dimerisation to 4,4′-dihydroxybibenzyl and is oxidised to the stilbenequinone.

Experimental confirmation of the isomerisation of the phenoxy-radical into the hydroxybenzyl radical was obtained by Brodskii and Pokhodenko[49,160,161], who studied the oxidation of 2,6-di-t-butyl-4-methylphenol containing deuterium in the methyl group. It was found that the oxidation of 2,6-di-t-butyl-4-methylphen[^{2}H]ol gives a dimeric product whose infrared spectrum, instead of the 2690 cm^{-1} band due to the stretching vibrations of the OD group, contains a band at 3650 cm^{-1} due to the OH group. This result shows that the primary act in the oxidation of 2,6-di-t-butyl-4-methylphenol involves the removal of hydrogen from the hydroxyl group, since the primary removal of hydrogen from the methyl group would have produced a dimer containing the OD group of the original phenol. An analogous result was obtained[161] in the oxidation of 2,6-di-t-butyl-4-perdeuteriomethylphenol. The infrared spectrum of the dimeric product was found to contain the band due to the stretching vibrations of the OD group, instead of the 3650 cm^{-1} band present in the original 2,6-di-t-butyl-4-perdeuteriomethylphenol. The results obtained in the works cited indicate isomerisation of the initially formed phenoxy-radical to produce the hydroxybenzyl radical, with transfer of hydrogen from the methyl group to the oxygen. These results also make it possible to reject the possibility of formation of benzyl radicals by the reaction of phenoxy-radicals with molecules of the original phenol according to the scheme proposed by Becconsall[51]:



The reaction of organic peroxides with trialkylphenols containing a methyl group in the *para*-position is interesting. The reaction of 2,4,6-trimethylphenol (XXVIII) and 2-t-butyl-4,6-dimethylphenol (XXIX) with peroxo-compounds gives the corresponding stilbenequinones as the final product[9]. On the other hand, the reaction of 2,6-di-t-butyl-4-methylphenol with peroxides gives cyclodienone structures of type (II)[10].

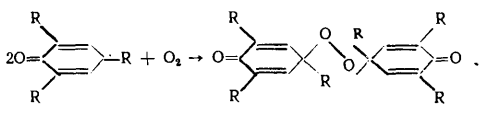
The only reaction of 2,6-di-t-butyl-4-methylphenol in which the formation of stilbenequinone is observed is that with triphenylmethyl hydroperoxide. This difference in the

behaviour of these phenols[9,10] can be explained as follows. The phenoxy-radical formed as a result of the primary attack of the peroxide residue on the phenol containing a methyl group in the *para*-position may react in two ways: in the first place, it may undergo isomerisation to an unstable hydroxybenzyl radical, whose dimerisation with subsequent oxidation of the dimeric products gives finally the stilbenequinone, or, in the second place, it may react with a new peroxide residue to give a cyclodienone derivative.

From the fact that the reaction of the phenols (XXVIII) and (XXIX) with peroxides gives stilbenequinones, it may be assumed that in this instance isomerisation takes place much more rapidly and more readily than their reaction with the peroxide residues. The phenoxy-radical formed in the oxidation of 2,6-di-t-butyl-4-methylphenol is much more stable than the phenoxy-radical formed in the oxidation of the phenols (XXVIII) and (XXIX), since both of its *ortho*-positions are occupied by bulky t-butyl groups. As a result, the rate of its isomerisation is decreased to such an extent that the main process leading to the disappearance of the radical is its reaction with the peroxide residues with the formation of cyclohexadienone structures of type (II). In the reaction with triphenylmethyl hydroperoxide, however, the rate of the reaction between the phenoxy-radical from the 2,4-di-t-butyl-4-methylphenol and the peroxide residue is decreased as a result of the marked steric hindrance of the reactive centre of the peroxide residue by the phenyl groups, and this prevents the reaction. The rate of this reaction is less than the rate of isomerisation of the phenoxy-radical to form the hydroxybenzyl radical, so that stilbenequinone is formed as the final reaction product.

The reaction of 2,6-di-t-butyl-4-methylphenol with alkyl nitrites, which readily decompose in solution to RO· and NO· radicals, leads to the corresponding quinonitrole (XXX) and hydroxybenzaldehyde (XXXI)[26]. To explain the formation of these products, a reaction mechanism which in our opinion is quite correct, was proposed[26]. The radical (X) formed as a result of the attack on the phenol molecule by the RO· radical either reacts with NO· with the subsequent formation of the quinonitrole or undergoes isomerisation to the hydroxybenzyl radical and then recombines with NO· to form the oxime of the corresponding hydroxybenzaldehyde; the oxime is readily converted into the aldehyde under the influence of the alkyl nitrite.

d. Reaction with oxygen. On contact with atmospheric oxygen, the usual bright blue or red colours of trialkylphenoxy-radicals gradually change to yellow, due to the formation of the bis-(1,3,5-trialkylcyclohexa-2,5-dienone) peroxides (XXXII)[27,28,30,46,64,65]. The formation of these peroxides is also observed in the oxidation of the phenols by PbO_2 or $K_3Fe(CN)_6$ in the presence of atmospheric oxygen:

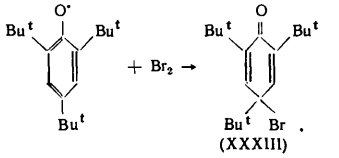


Proof of this structure for the peroxo-compounds is provided by the fact that the infrared spectra contain a doublet at 6.0 μm and 6.2 μm, corresponding to the quinonoid structure, and do not contain the band due to the hydroxyl group of the original phenols.

When the products of the reaction of phenoxy-radicals with oxygen are treated with hydriodic acid or sodium iodide in acetic acid, free iodine is liberated, indicating that they contain the peroxo-group O–O [50].

The ease of formation of bis-peroxides from phenoxy-radicals depends on the type of substituent in the *para*-position of the radical. Thus the rate of the reaction of 2,6-di-t-butylphenoxy-radicals with oxygen decreases with change in the substituents in the following order[36]: C_6H_5 > > $(C_6H_5)_3C$ > C_6H_5CO > C–N. A decrease in the rate of the reaction of phenoxy-radicals with oxygen is also observed when the t-butyl group in the *para*-position of the radical is replaced by methylphenyl or naphthyl groups, due to the additional stabilisation of the radical resulting from delocalisation of the unpaired electron[36,163]. An interesting feature is that the rate of the reaction with oxygen for the radical in which the *para*-position is occupied by the *p*-methylphenyl group is only half the rate of the reaction of the radical containing the *o*-methylphenyl group in the *para*-position[163]. This increase in reaction rate is apparently due to the decrease in the stability of the radical containing the *p*-methylphenyl group as a result of its displacement from the coplanar state, leading to the loss of conjugation energy.

e. Reaction with halogens. The addition of bromine solution to a solution of the 2,4,6-tri-t-butylphenoxy-radical in the absence of atmospheric oxygen produces a yellow crystalline precipitate[28], whose infrared spectrum[46] does not contain the band due to the hydroxyl group, but contains a double band at 6.0 μm and 6.2 μm, corresponding to the quinonoid structure (XXXIII):



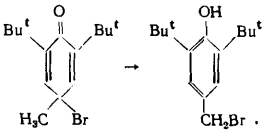
(XXXIII)

Compound (XXXIII) is also formed by the reaction of the phenol itself with bromine[164]. Study of the bromination of a number of phenols showed that in all instances the products are *p*-quinonoid structures, even when attack at the *ortho*-position is less hindered than attack at the *para*-position. This phenomenon is explained by the fact that electrophilic substitution in the phenol series takes place with a much smaller activation energy in the *para*-position than in the *ortho*-position[164].

All the quinobromides isolated have an absorption maximum in the range 248–251 nm, confirming the formation of the *p*-quinonoid structure (*o*-quinonoid structures have an absorption maximum in the range 320–360 nm [164]).

The stability of the quinobromides depends to a marked extent on the size of the substituents. Thus mesitol quinobromide exists for only 8 min at 20°C, whereas 2,6-di-t-butyl-4-methylphenol quinobromide exists for several days[162].

The instability of quinobromides with a methyl group in the *para*-position is due primarily to their spontaneous rearrangement with transfer of the bromine from the benzene ring to the methyl group



At elevated temperatures in the solid state and in non-polar solvents, this rearrangement takes place by a radical mechanism[72].

The reaction of phenoxy-radicals with (dichloroiodo)-benzene or with free chlorine gives quinochlorides similar

to the quinobromides described above. These compounds are unstable, and when heated they liberate chlorine and the original phenoxy-radicals.

f. Dehydrogenation of phenoxy-radicals. An extremely characteristic reaction of phenoxy-radicals, as of other free radicals, is the removal of hydrogen from organic compounds; the hydrogen becomes attached to the oxygen atom of the phenoxy-radical, and the radical formed from the molecule donating the hydrogen often recombines with the original phenoxy-radical with the formation of a quinol ether [165,166]. An example is the reaction of phenoxy-radicals with aromatic aldehydes [12] and with oximes of various structures [167].

The reaction of phenoxy-radicals with hydroperoxides leads to decomposition of the latter with the formation of stable products, and this is of considerable importance for processes of inhibited oxidation. The hydroperoxides in this instance cannot initiate new oxidation chains. Study of the kinetics of the disappearance of the 2,6-di-t-butyl-4-(3′,5′-di-t-butyl-4-hydroxydicyclohexa-2′,5′-dienylidenemethyl)phenoxy-radical in the presence of propene hydroperoxide [168] showed that the reaction is of first order with respect to each component. A bimolecular reaction mechanism with first-order kinetics with respect to each component was also found [169] in a study of the reaction of the 2,4,6-tri-t-butylphenoxy-radical with t-butyl hydroperoxide. The 2,4,6-tri-t-butylphenoxy-radical also removes a hydrogen atom from diethyl phosphite molecules. On the basis of kinetic data it was shown [170] that the reaction with diethyl phosphite involves the removal of hydrogen from the P–H bond of the monomeric form of the phosphite.

Stable phenoxyl radicals readily dehydrogenate phenols. An example is provided by the reaction of the 2,4,6-tri-t-butylphenoxy-radical (ArO·) with 4-t-butylphenol (PhOH) [171]. The observed ratio of the reacting components (2 moles ArO· per mole of PhOH) corresponds to the following reaction scheme:

$$\underset{\text{stable}}{ArO^{\cdot}} + PhOH \rightleftarrows ArOH + \underset{\text{unstable}}{PhO^{\cdot}}$$

$$ArO^{\cdot} + PhO^{\cdot} \underset{\text{slow}}{\overset{\text{rapid}}{\rightleftharpoons}} ArOOPh$$

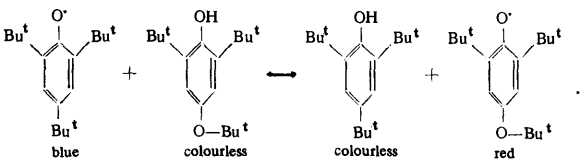
$$2ArO^{\cdot} + PhOH \rightarrow ArOH + ArOOPh$$

The formation of the quinol ether was also observed [172] in the reaction of the 2,6-di-t-butyl-4-phenylphenoxy-radical with 2-naphthol.

All the quinol ethers obtained are unstable. When heated in organic solvents they undergo reversible dissociation to the original radicals. The rate of dissociation is greater, the more marked the screening of the hydroxyl group of the phenol. Thus the quinol ether formed by diphenylnitroxide and the 2,4,6-tri-t-butylphenoxy-radical, formed by removal of a hydrogen atom at 20°C by the 2,4,6-tri-t-butylphenoxy-radical, undergoes reversible dissociation to the extent of 1%. [66]

The reaction of stable phenoxy-radicals with sterically hindered phenols in which the *para*-position is free or contains halogens, produces other reaction products [173]. For example, the reaction between the 2,4,6-tri-t-butylphenoxy-radical and 2,6-di-t-butylphenol leads to condensation of the benzene rings of the latter with subsequent dehydrogenation of the dimeric products and the formation of the corresponding diphenoquinone. The reaction of 2,6-di-t-butyl-4-methylphenol with stable radicals is analogous [143].

The reaction of stable phenoxy-radicals with phenols which also give stable radicals on dehydrogenation is an equilibrium reaction of the type:



The equilibrium constant for this reaction at 25°C is 51.7 ± 4.1, [35] that is, for the same initial concentrations of the components, the equilibrium is displaced towards the formation of the more stable alkoxyphenoxy-radical.

The same equilibrium reaction with the 2,4,6-tri-t-butylphenoxy-radical is undergone by 2,6-di-t-butyl-4-methoxyphenol [174] and 2,4,6-triphenylphenol [151].

Kreilick and Weismann [175] used the NMR method to determine the rate constant for the reaction of the 2,4,6-tri-t-butylphenoxy-radical with a molecule of the corresponding phenol, from the broadening of the signal due to the protons of the hydroxyl group. The rate constant found in this way at 30°C in CCl_4 was 300 litre mole^{-1} s^{-1}, and the value found for the activation energy was 1.0 ± 0.5 kcal mole^{-1}.

On the basis of a study of a large number of dehydrogenations, Muller and coworkers [176] suggested that the first stage in the dehydrogenation of organic compounds by phenoxy-radicals is the formation of an ion pair (A), stabilised with the formation of a new radical (B), which subsequently undergoes further transformation:

$$ArO^{\cdot} + HXR \rightleftarrows \underset{(A)}{[Ar\bar{O}\cdots H\cdots \overset{+}{X}R]} \rightleftarrows \underset{(B)}{ArOH} + RX^{\cdot}.$$

The dehydrogenation of various organic compounds by stable radicals provides a convenient method for studying the reactivity of these compounds. Kinetic studies of dehydrogenation by stable radicals make it possible to estimate the part played by energetic and steric factors in kinetics and to reach conclusions regarding the reaction mechanism. Here, promising possibilities are provided by the EPR method.

Buchachenko and coworkers [177] have used this method to study the reactivity of C–H bonds in various hydrocarbons with respect to the 2,4,6-tri-t-butylphenoxy-radical. It was found that in the hydrocarbon series n-decane–trimethylheptane and toluene–ethylbenzene–cumene, it is possible to follow the influence of methyl groups on the reactivity of the C–H bond being attacked, and in the series toluene–diphenylmethane it is possible to follow the influence of phenyl groups. The data obtained indicate that the reaction of the 2,4,6-tri-t-butylphenoxy-radical with hydrocarbons is characterised by relatively high activation energies, due to the endothermic nature of the removal of hydrogen, and that the activation energy decreases regularly with decrease in the strength of the C–H bond being attacked, from n-decane to diphenylmethane. Comparison of the activation energies in the toluene–diphenylmethane series shows that the introduction of phenyl groups has a much more marked influence on the kinetics of the process than the introduction of methyl groups. Examination of the values of the pre-exponential term (K_0) and entropy of activation ($\Delta S^{\neq}$) revealed the screening influence of the methyl and more particularly the phenyl groups, leading to a decrease in the probability of formation of the activated complex.

The 2,4,6-tri-t-butylphenoxy-radical has also been used to study the reactivity of the OH bonds in nitrophenols and the influence of solvents on this reaction[178].

The data obtained indicate that when nitro-groups are introduced into the phenol molecule, the activation energy for the removal of hydrogen from the hydroxyl group of the phenol is increased, but when several nitro-groups are introduced the effect is not additive. Measurement of the rate constants for the removal of hydrogen from *o*-nitrophenol in hexane, benzene, acetone, or methanol showed that the rate constant is independent of the nature of the medium. In the opinion of the authors cited[178], this indicates that the phenol taking part in the reaction is not solvated, apparently because of steric hindrance, in contrast to *m*-nitrophenol, which forms stable hydrogen bonds with the solvent.

As already noted, the thermal decomposition of the peroxide of the substituted cyclodienone (III) and ionol hydroperoxide (VII) is accompanied by the formation of phenoxy-radicals. It has been shown by the EPR method that these radicals are capable of removing hydrogen from the OH and NH groups of sterically hindered phenols.

The kinetics of the reaction of the stable tetra-t-butylindophenoxy-radical (XVII) with various aromatic amines and phenols were studied recently[179,180]. These compounds were chosen in order to study the influence of steric factors on the rate of hydrogen transfer, and also to study the influence of substituents and the applicability of the Hammett equation to radical reactions of this type.

Comparison of the activation energies, pre-exponential terms, and entropies of activation for the reaction of (XVII) with diphenylamine (DPA) and aniline shows that the replacement of one hydrogen atom in the NH_2 group of aniline by a phenyl group does not alter significantly the stability of the bond being attacked: the activation energy changes only slightly on going from aniline to DPA. The pre-exponential term, however, decreases by two orders of magnitude (the entropy of activation, which is a measure of the probability of formation of the active complex, decreases by 8 e.u.), indicating marked steric hindrance by the phenyl group. Thus the decrease in the rate constant for the reaction with DPA relative to the reaction with aniline is due to steric hindrance of the reactive centre of the DPA molecule by the two phenyl groups. A similar marked steric hindrance by the phenyl group was also observed[177] in a study of the removal of hydrogen from toluene and diphenylmethane by the 2,4,6-tri-t-butylphenoxy-radical.

The kinetics of the reaction of the radical (XVII) with aniline and its *para*-derivatives were studied[180] to investigate the influence of substituents on the reactivity of the NH bond in anilines. The values found for the rate constants for this reaction show that electron-donating substituents in the *para*-position of aniline increase the rate of removal of hydrogen, whereas electron-accepting substituents decrease the rate of hydrogen removal. The values of the logarithms of the reaction rate constants as functions of the corresponding values of the Hammett constants σ lie satisfactorily on a straight line, whose slope gives a value for ρ equal to 2.58. This high value of ρ indicates the importance of the polar influence of the substituents on the rate of removal of hydrogen from the NH bond of amines. A study of the rate of removal of hydrogen from DPA and aniline labelled with deuterium in the amino-group showed the existence of isotopic effects k_H/k_D, indicating that the stage determining the rate of the radical reaction of hydrogen removal is the rupture of the NH bond in the amine.

To investigate the influence of polar and steric factors on the reactivity of phenols, a study was made[179] of the reaction of the radical (XVII) with 2,6-di-t-butyl-4-R-phenols and phenols which did not contain alkyl substituents in the *ortho*-positions.

The reaction was carried out at phenol concentrations in the range 10^{-4}–10^{-3} M, in which displacement of the band due to the monomeric form of the OH group of the phenol in the infrared spectra is not observed. On this basis the results of the study were related to non-associated phenol molecules.

The data obtained show that on going from *ortho*-unsubstituted phenols to 2,6-di-t-butyl-4-R-phenols the pre-exponential term decreases by more than two orders of magnitude, corresponding to a decrease in the entropy of activation by 6 e.u. This indicates marked screening of the O–H group of the phenols by the two ortho-t-butyl groups. Despite this, the rate of transfer of hydrogen to the radical (XVII) from the 2,6-di-t-butyl-4-R-phenols is much greater than that from *ortho*-unsubstituted phenols. Comparison shows that the activation energy for the reaction of the radical (XVII) with sterically hindered phenols is only one-third of that with *ortho*-unsubstituted phenols. Thus in the reaction of the radical (XVII) with sterically hindered phenols there is a strong compensation effect, so that in spite of the marked screening action of the two *ortho*-t-butyl groups on the OH bond of the sterically hindered phenols, these groups at the same time alter the properties of the OH bond being attacked to such an extent that the transition state of the reaction is realised with a smaller expenditure of energy for 2,6-di-t-butyl-4-R-phenols than for *ortho*-unsubstituted phenols. For this reason the reactivity of sterically hindered phenols in the transfer of hydrogen to a stable radical is greater than that for *ortho*-unsubstituted phenols.

The rate of transfer of hydrogen to the radical (XVII) decreases in the order 2,6-di-t-butylphenol–2,6-di-t-butyl-4-methylphenol–2,6-di-t-butyl-4-ethylphenol, and the electron-donating properties of the substituents in the *para*-position increase in the same order.

Comparison of the rate constants for the reactions of the radical (XVII) with diphenylamine and phenols shows that the rate of the reaction with diphenylamine is less than that with phenols by a factor of 100–1000. This is due to the marked hindrance of the reactive centre in DPA and its derivatives, resulting in lower values of the pre-exponential term, compared with phenols. Similar low values of the pre-exponential terms were previously observed in the reaction of DPPH with a number of amines[66].

Practical requirements in the development of new and effective phenolic inhibitors of radical reactions should be turning the attention of research workers primarily to the study of the influence of the steric and polar properties of substituents on the stability and reactivity of the radicals formed in the oxidation of sterically hindered phenols, since detailed information in this field will open up new perspectives in the scientific selection of substances capable of retarding undesirable changes in organic compounds chiefly polymers, during their exploitation.

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Retention of Configuration in Reactions with Opening of an Epoxide Ring

A. A. Akhrem, A. M. Moiseenkov, and V. N. Dobrynin

Information on the opening of an epoxide ring with retention of the initial configuration under conditions of catalytic hydrogenation and under the action of various nucleophilic reagents is examined. It is noted that when an electron-donating *p*- or π-grouping is present in the α position to the epoxide ring the retention of the initial configuration is more probable than its inversion. Bibliography of 182 references.

CONTENTS

I. Introduction 448
II. Some general features of the chemistry of epoxides 448
III. Stereochemistry of epoxide ring opening proceeding with retention of the configuration 449
A. Epoxy-compounds in which the effect of conjugation is absent 449
B. Epoxy-compounds in which the effect of conjugation appears. 451

I. INTRODUCTION

A large number of reactions of epoxides with various reagents has now been studied. The great mass of results that had accumulated were summarised in several exhaustive reviews[1-6], and the most recent of these also dealt with the stereochemical aspect of the transformations. In 1951 Fürst and Plattner[7] formulated the "rule for the biaxial opening of the expoxide ring", which three years later Cookson[8,9] and Angyal[10] extended its applicability from the position of conformational analysis to cyclic systems. According to these ideas, the opening of the oxide should be accompanied by inversion of the configuration of one of the carbon centres of the three-membered ring. However, at approximately the same time publications appeared showing that in several instances opening of the epoxide ring takes place with retention of the original configuration. An analysis of the constantly increasing number of experimental results shows that the so-called "sterically anomalous (*cis*-)opening of an epoxide ring" is observed among various representatives of the class of oxide compounds when various reagents act on them. The present review considers those instances which have not yet been summarised in the literature and covers information published up to July 1966.

II. SOME GENERAL FEATURES OF THE CHEMISTRY OF EPOXIDES

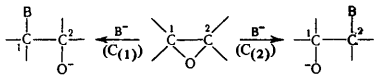
In the reviews mentioned above the correctness of the following general features of the chemistry of epoxides has been demonstrated convincingly.

1. The epoxide group often reacts in two ways, interacting with both electrophilic and nucleophilic agents under definite conditions. However, information on reaction with the latter predominates in the literature. The changes in the presence of electrophilic and radical reagents, and also on irradiation, lead mainly to the formation of products of various rearrangements of the oxide ring.

2. Breaking of the C–O bond of the epoxide takes place under the influence of various agents. Breaking of the C–C bond of the oxide ring is improbable and is observed only in the presence of strongly electronegative substituents, as occurs, for example, for oxides of cyclic trienes[11] and pentaenes[12], tetracyanoethylene oxide[13], etc.

3. The mechanism of the opening of the epoxide under the action of a nucleophilic reagent depends on the electronic and steric properties of the two reagents and on the reaction conditions. The results of the opening of the oxide are usually explained by schemes of the unimolecular and bimolecular substitution type. The direction of

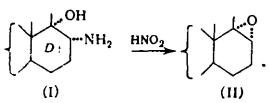
the opening of unsymmetrically substituted epoxides depends on the above factors and in general the formation of two structural isomers is possible:



The ratio of the latter cannot be predicted, although in some particular instances useful empirical relations exist.

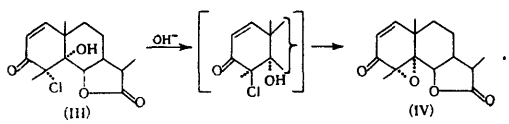
4. The stereochemistry of the opening of epoxy-compounds is determined by the steric rules for the occurrence of S_N1 and S_N2 processes. The stereochemical requirements for an S_N2 mechanism arise in the formation of a *trans*-coplanar transition state as a result of axial attack by the nucleophilic reagent on one of the carbon atoms of the epoxide with subsequent inversion of the configuration of the centre being attacked. In the cleavage of the epoxide ring by an S_N1 type mechanism as a result of the interaction with the nucleophilic reagent formation of products with both retention and inversion of the initial configuration can be expected.

5. A necessary condition for the closing of an epoxide ring is the coplanar antiparallel location of the attacking and leaving substituents. However, some departures from the classical scheme of closing of an epoxide ring are known. Thus Shoppee and coworkers[14] found that on treating the D-homopregnane amino-alcohol (I) with nitrous acid the α-oxide (II) is obtained in good yield. The explanation for this type of closing of the oxide ring is that the OH group of the *cis*-*e*, *a*-amino-alcohol (I) is in a position convenient for the formation of a pyramidal transition state, and consequently the removal of the diazonium group proceeds as a result of a synchronous process of the pinacoline type without formation of an intermediate carbonium ion.



(I) (II)

Moreover, it is known that in the diazotisation of *threo*-1,2-diphenyl-2-aminoethanol the oxide of *trans*-stilbene is produced in low yield[15]. The retention of the initial configuration is also observed in the treatment of the *cis*-chlorohydrin (III) with alkali[16]. However, here it is suggested that the ketol (III) is first isomerised by a retro-aldolisation type of mechanism into an intermediate *trans*-chlorohydrin, which is then converted into the keto-oxide (IV):



(III) (IV)

A similar process evidently takes place in the series of diastereoisomeric esters of α-chloro-β-hydroxy-β-trifluoromethylpropionic acid, which give only one epoxypropionate on treatment with sodium hydride[17].

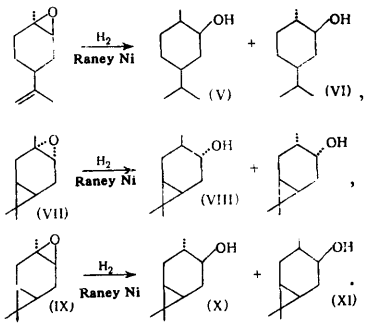
III. STEREOCHEMISTRY OF EPOXIDE RING OPENING PROCEEDING WITH RETENTION OF THE CONFIGURATION

It must be noted that the presence in the literature of isolated information on the "sterically anomalous" opening of an oxide ring, and also the absence, with a few exceptions, of systematic investigations in this field still do not allow a satisfactory classification to be given for all instances of this interesting phenomenon. Nevertheless we can provisionally distinguish two large groups of epoxy-compounds in which this phenomenon is observed.

A. Epoxy-Compounds in which the Effect of Conjugation is Absent

The *cis*-opening of the oxide ring in this group of compounds is encountered extremely rarely and is characteristic for the conformationally rigid secondary-tertiary and ditertiary cyclic epoxy-compounds. It is therefore quite probable that in all the examples considered below the steric factor plays a paramount part.

1. Reductive *cis*-opening of an oxide ring. Examples are known when the catalytic hydrogenation of cyclic epoxides leads to cleavage products with retention of the configuration of the initial oxides. Evidently such conversions were first observed by Brunel[18,19] and Kötz and Hoffman[20] in studying the hydrogenation of methylcyclohexene oxides in the presence of nickel and platinum catalysts. According to their results, for example, 1-methylcyclohexene oxide gives *trans*-2-methylcyclohexanol. This result signifies that the entry of hydrogen and the breaking of the C–O bond probably occur at the same side of the cyclohexane molecule, which also ensures the *cis*-opening of the oxide ring. On the basis of an analysis of the complex mixture of products obtained in the hydrogenation of 1,2-, 2,3-, and 3,4-epoxymethanes in the presence of palladium hydroxide, Pigulevskii and Kozhin[21] assumed the similar possibility of the retention of the configuration of the original oxide as did Kergomard and Geneix[22,23], who studied the catalytic hydrogenation of tetrahydromyrcene oxide, pinene oxide, carbomenthene oxide, and limonene oxide. It was recently shown that the products of the hydrogenation of the sterically homogeneous *trans*-*p*-menthadiene oxide contain not only neoisocarbomenthol (V) but also carbomenthol (VI),[24,25] which arises as a result of the *cis*-opening of the epoxide ring.

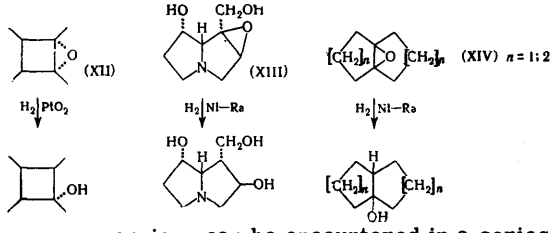


(V) (VI) (VII) (VIII) (IX) (X) (XI)

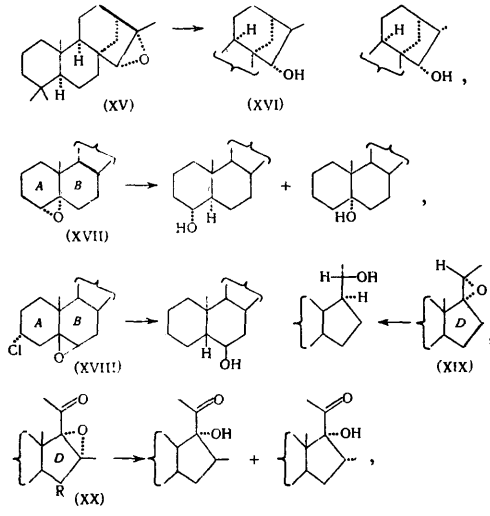
Similar results are obtained in investigating the hydrogenation of isomeric carene oxides (VII) and (IX) over Raney nickel catalyst under pressure[26]. Here with the oxide (VII) there is 82% *cis*-opening of the epoxide ring—formation of product (VIII)—and with oxide (IX) the products of the *cis*- and *trans*-opening, (X) and (XI), are formed in approximately equal amounts.

Retention of the initial configuration is observed in the catalytic hydrogenation of epoxytetramethylcyclobutane

(XII)[27] and of the oxides of the bicyclic alkenes (XIII)[28] and (XIV)[29].

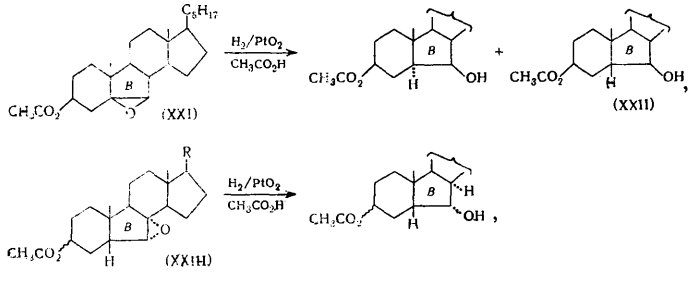


Analogous conversions can be encountered in a series of polycyclic epoxy-compounds. Thus isophyllocladene oxide (XV) in the presence of Adams catalyst gives a mixture of epimeric alcohols with a preponderance of the product of *cis*-cleavage (XVI)[30]. Under the same conditions 4α,5α-epoxycholestane (XVII) is converted into a mixture of approximately equal amounts of the 4α- and 5α-alcohols[31], whereas only the 6β-alcohol is obtained from 3α-chloro-5β,6β-epoxycholestane (XVIII)[32]. Furthermore, exclusively *cis*-opening is observed[33,34] in the catalytic hydrogenation of pregnane 17α,20α-oxides (XIX) over Raney nickel. As regards the ditertiary pregnane keto-acids (XX) in the presence of a palladium catalyst they undergo either partial or complete *cis*-opening, depending on the hydrogenation condition[35,36]:



where R = H or Br.

Recently, Šorm and coworkers[37,38] described the opening of oxides of the B-norcholestane and B-norandrostane series. Here the 5β,6β-oxide (XXI) gave a mixture of alcohols with a considerable preponderance of product (XXII), which exhibits the configuration of the original epoxide. With the 6α,8α-oxide (XXIII) the opening proceeds exclusively with retention of the original configuration

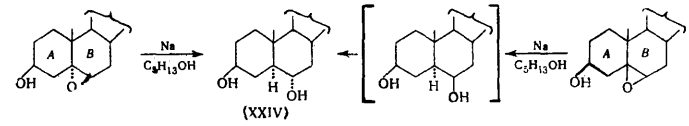


where R = C_8H_{17}, O_2CCH_3.

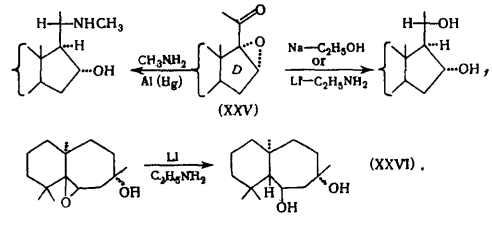
To explain the conversions mentioned it is necessary to assume that the generally accepted ideas about the mechanism of catalytic hydrogenation of steroidal alkenes[39] are also applicable to steroidal epoxides.

It is extremely probable that here also the reaction proceeds by *cis*-addition of a molecule of H_2, adsorbed on the surface of the catalyst, to the sterically most accessible C–O bond of the oxide ring.

cis-Opening is much more rarely encountered for other methods of reducing the oxides. Thus, Urushibara and Chuman[40] observed the reduction of 5α,6α-oxides of cholesterol by sodium in pentyl alcohol to give the 3β,6α-glycol (XXIV):



They obtained the same product in identical conditions from cholesterol 5β,6β-oxide. However, it appeared that initially there is *trans*-opening of the cholesterol β-oxide to the intermediate 3β,6β-glycol, which subsequently isomerises to the more stable 6α-epimer under the conditions of the redox reaction. It is also known that the reductive amination of the steroidal 20-keto-16α,17α-oxides (XXV) is accompanied by their *cis*-opening[41]. The same result is observed in the reduction of oxides (XXV) by sodium in alcohol[42] or by lithium in ethylamine[43]. With the aid of the last reagent Widdrol β-oxide† was converted into the glycol (XXVI) in ~ 40% yield[44].

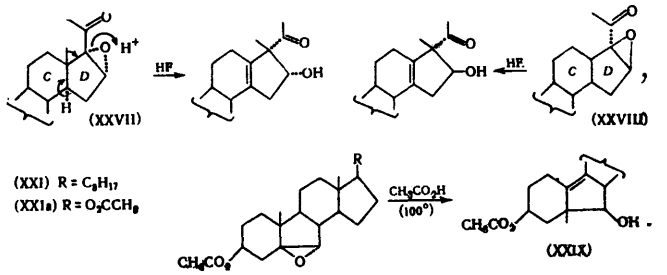


2. Oxides in Wagner–Meerwein type rearrangements. The reaction of cyclic secondary-tertiary and ditertiary oxides with acids, just like the epoxidation of the corresponding alkenes, often leads to the formation of products of various rearrangements[3,6]. It is usual to explain these conversions by the concept of the carbonium-ion intermediate, the manner of the "neutralisation" of which determines the structure of the final products. Sometimes these can be products of a Wagner–Meerwein type rearrangement. It is well known that the latter includes the simultaneous formation of an electron-deficient centre and an antiparallel *cis*-1,2-displacement of the migrating substituent (usually methyl), that for an epoxide will signify its *trans*-opening. Such a situation is preferable, since this process does not result in the formation of a discrete carbonium ion. However, it is possible for there to be a non-simultaneous process including the anticipatory stage of the formation of a stable carbonium ion at the site of the rupture of the C–O bond of the oxide ring[45,46]. The latter implies that with the mutual *cis*-arrangement of the epoxide and migrating groups the configuration of the two carbon centres of the original oxide will be retained. Both these types of mechanism

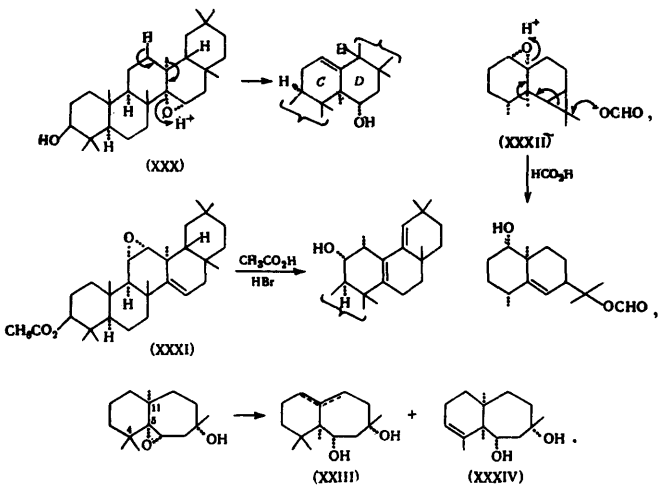
† The symbols α and β in the present review signify, as in steroids, the configuration of the three-membered oxide ring.

are observed experimentally, as is illustrated by the conversion of isomeric keto-oxides of the pregnane series (XXVII) and (XXVIII)[47,48].

On the other hand, on heating the 5β,6β-oxides (XXI) and (XXIa) in acetic acid *cis*-opening takes place exclusively[37], and the formation of 19,B-bis-nor-products (XXIX) does not have an analogy in the normal steroidal series which contains a six-membered ring B.



The literatures also describes the "anomalous" opening of terpene epoxides in the presence of acids, as is shown by the examples of taraxerine oxides (XXX)[49] and (XXXI)[50] and calarene oxide (XXXII)[51]:

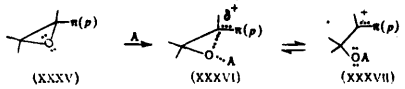


An interesting example is Widdrol α-oxide itself, which on boiling in water gives a mixture of homoallyl alcohols (XXIII) and (XXXIV)[44]. It is suggested that the configuration at $C_{(5)}$ is retained as a result of the formation of an hydrated carbonium-ion intermediate which is subsequently stabilised by a displacement of the methyl group at $C_{(4)}$ or $C_{(11)}$.

B. Epoxy-Compounds in which the Effect of Conjugation Appears

To this group belong the compounds in which the oxide ring is adjacent to an unsaturated bond or to an atom with an unshared *p*-pair of electrons. Like conjugated cyclopropanes and aziridines, the epoxy-compound (XXXV) displays the conjugation, as is shown by the ultraviolet spectra of monoepoxides of conjugated dienes[52], aryl oxides[53] and keto-oxides[54]. However, it must be stated that the investigation of infrared spectra of acyclic keto-oxides[55] and epoxypropionates[56] did not disclose any appreciable conjugation between the oxide ring and the C=O group, although this effect probably occurs to an insignificant extent in several cyclic keto-oxides[57].

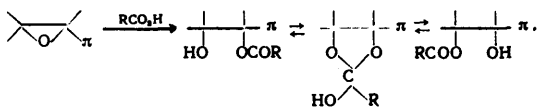
The greatest number of examples of *cis*-opening have been described for epoxides of the type of (XXXV). In all these examples, except for the reaction of indene oxide[58] and phenylcyclohexene oxide[59] with dilute alkali and also the reduction of certain oxides by alkali metal complex hydrides[60-62] or by lithium in ethylamine[63] the reaction takes place under conditions of electrophilic catalysts. According to generally accepted ideas, under such conditions partial or complete rupture of the C–O bond of the epoxide is possible with formation of cationic intermediate transition states (XXXVI) and (XXXVII):



where $\pi(p)$ is aryl or ester; and A is a Lewis acid.

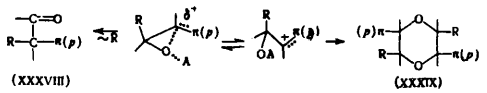
Here it is considered that the existence of this type of transition state is the main reason determining the "sterically anomalous" opening of the oxide ring (XXXV). A similar approach to the solution of the problem under discussion is justified by the following observations.

1. The primary change leading to products of the *cis*-opening of the oxide ring takes place at the carbon atom connected to the electron-donating substituent. This is not always evident for the reactions of oxides with carboxylic acids owing to the frequently observed secondary process of the migration of the acyl residue and the possible formation of a mixture of monoesters[59,64-71]:



To show the direction of attack of the nucleophilic reagent it is convenient to use an acid the acyl residue of which exhibits reduced tendency to migration, for example, mesitylenecarboxylic acid[65,66]. The determination of the direction of acid hydrolysis of the epoxy-compounds (XXXV) is more complex. Definite results in this instance can be obtained with the aid of optically active substances, as was done for styrene oxide[65] and phenylpropene oxide[72].

2. The opening is often accompanied by the formation of carbonyl products (XXXVIII), which arise as a result of the rearrangement of the epoxide under the action of electrophilic catalysts[3,6]. Sometimes such a direction for the reaction predominates, this being especially characteristic for oxides of type (XXXV). Under certain conditions stabilisation of the new electron-deficient centre can be brought about by dimerisation (XXXIX), as for example, with 3-methoxydihydronaphthalene oxide[73,74]:



where R = H, alkyl, aryl, acyl.

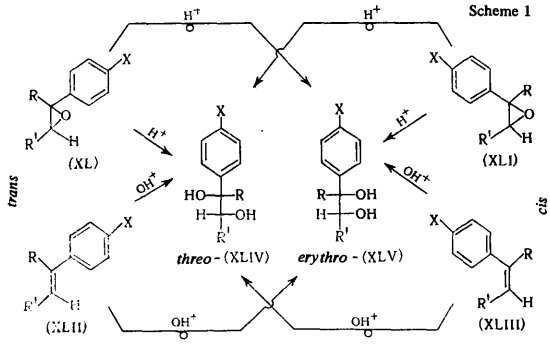
3. Kinetic investigations show that the opening of the oxide (XXXV) can be described by either S_N2 or S_N1 mechanisms with each of these taking part in different proportions in any particular instance[3,6]. In this connection the production of a mixture of products with inversion and retention of the configuration of the reaction centre can be expected. The *cis*-opening of the oxides (XXXV) is usually connected with the possibility of unimolecular substitution, although this viewpoint has been criticised[2,3].

1. *cis*-Opening of Aryloxides. The account of the information on the *cis*-opening of one of the most widely studied groups of epoxides of type (XXXV)—the aryl-

oxides—must begin with consideration of some of the conversions of styrene oxide, although in view of the primary–secondary nature of the latter the stereochemistry of these changes cannot be discussed conclusively. For example, it is found that the attack of carboxylic acids[64,65,67] and hydrogen halides[67,75-78] is directed preferentially at the benzyl carbon atom and the products of the reaction of optically active styrene oxide with weak acids (benzoic and mesitylenecarboxylic) are racemates. On treatment with trichloroacetic (in benzene), acetic, and dilute sulphuric acids, and also with phenylmercaptoborane[79] (in tetrahydrofuran) inversion is observed, equal respectively to 37, 62, 66, and 85%. On this basis it was suggested[65,67,79] that opening of styrene oxide, which is catalysable by weak acid, proceeds preferentially by an S_N1 mechanism with formation of a rather stable intermediate benzyl carbonium ion.

With the appearance in the molecules of styrene oxides a second asymmetric centre it seems possible to consider definitely the stereochemistry of the opening of the epoxide ring as a process depending on the steric and electronic factors of the substituents, the nature of the attacking agent, etc. In the general form, such opening is represented in scheme I by hydrolysis of the isomeric oxides (XL) and (XLI), and also by the equivalent epoxidation of alkenes (XLII) and (XLIII) by some certain per-acids. In this the "sterically anomalous" process in a series of *trans*‡-compounds (XL) and (XLII) should lead to *threo*-glycols (XLIV), but in the *cis*§-systems (XLI) and (XLII), to the *erythro*-glycols (XLV). Böeseken and coworkers[80,81] evidently were the first to observe such changes; they isolated a mixture of monoacetates of racemic and meso hydrobenzoins in the epoxidation of stilbenes (XLII, XLIII; R = X = H; R′ = C_6H_5). Analogous results on the opening of aryl oxides and the epoxidation of the corresponding alkenes obtained by other authors are summarised in Table 1.

Scheme 1



The data in this table show that in a comparatively non-polar medium the predominating direction of the opening of the *trans*-oxides (XL) by acids is, like the addition of the elements of per-acids to *trans*-alkenes (XLII), "sterically anomalous". In the *cis*-series (XLI, XLIII) these reactions are characterised by a lower degree of stereospecificity, and moreover the yield of final products is somewhat less. In almost every instance carbonyl compounds are observed as side-products, their formation depending to a considerable extent on the pH of the medium. For example, the amount of 4-methoxybenzyl phenyl ketone is increased threefold when the reaction of *trans*-4-methoxystilbene with $C_6H_5CO_3H$ takes place in benzene saturated with water (Table 1, Nos. 21 and 22). When a non-polar solvent is used the pH of the medium has little effect on the yield of products with retained configuration (Table 1, Nos. 9–16) but considerably affects the rate of the process. Thus for the opening of *trans*-stilbene oxide chloroacetic acid (p*K* 2.81) requires the reaction mixture to be boiled for several hours, whereas with trichloroacetic acid (p*K* 0.1) the reaction is completed in the cold in a few minutes (in benzene)[86,87]. Probably the increased reaction rate in the presence of a strong acid can also explain the formation of trichloroacetates of hydrobenzoins (instead of benzoates) in the epoxidation of stilbenes by an equimolecular mixture of perbenzoic and trichloroacetic acids (Table 1, Nos. 17, 18, 33).

The data in Table 1 show that *cis*-opening of the oxide ring of the systems being considered is evidently not characteristic in a strongly polar medium. For example, acid hydrolysis and acetolysis of isomeric oxides of methylstyrene (XL, XLI; R = X = H, R′ = CH_3), or the epoxidation of the corresponding alkenes (XLII, XLIII) with performic acid leads predominantly to products with inverted configuration (Table 1, Nos. 1–8). Similarly, the acid hydrolysis of *trans*-anisyltolylethylene (XL; R = H, X = OCH_3, R′ = *p*-$CH_3C_6H_4$) gives a mixture of diastereoisomeric glycols (Table 1, No. 26), whereas treatment with benzoic acid in chloroform (rather low polarity) results in full retention of the configuration (Table 1, Nos. 25).

Instances of the stereospecific opening of aryl oxides irrespective of the polarity of the medium have been described. Thus, it is known that acid hydrolysis of the secondary-tertiary *trans*-α-methylstilbene oxide (XL; R = CH_3, X = H, R′ = C_6H_5) gives *threo*-α-methylhydrobenzoin[90-92]. Complete retention of the initial configuration i observed in the opening of the same oxide under milder con ditions, and also in the epoxidation of the corresponding *trans*-alkene (XLII; R = CH_3, X = H, R′ = C_6H_5) (Table 1, Nos. 29–33).

The effect, mentioned above, of the polarity of the solvent on the nature of the opening of the epoxide ring is illustrated by the celebrated examples of the reaction of hydrogen halides with aryl keto-oxides, β-phenylepoxypropionates, and stilbene oxides. Thus, Jorlander[93] found that, depending on the solvent used (alcohol or acetic acid), 1-anisyl-2,3-epoxy-3-phenylpropan-1-ol forms various chlorohydrins with hydrogen chloride. Later it was shown by other examples that such compounds are not structural isomers. Moreover it was found that in every instance the halogen atom is attached in the β position to the C=O group and that frequently such addition proceeds with retention of the configuration of the original oxide (Table 2).

As Table 2 shows, when hydrogen halides react with disecondary carbonyl-containing phenyl oxides (XLVI) and (XLVII) in non-polar solvents there is a stereospecific *cis*-opening of the epoxide ring, whereas in polar media there is complete inversion of the configuration (Table 2, Nos. 1, 2, 12, 13). With the secondary-tertiary dypnone oxide and *cis*-bromodiphenacyl oxide, irrespective of the polarity of the solvent there is a "sterically anomalous" reaction (Table 2, Nos. 6, 7, 10, and 11). In this respect these epoxides behave completely analogously to the *trans*-α-methylstilbene oxide (XL; R = CH_3, X = H, R′ = C_6H_5) mentioned above.

The stereospecific *cis*-opening of the oxides (XLVI and XLVII) proceeds in the presence of Lewis acids (Table 2, Nos. 3–5, 8, and 9). When using boron trifluoride–diethyl

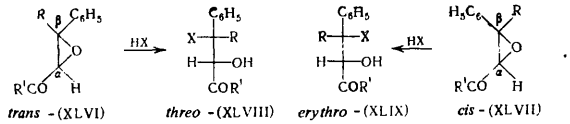
† Relative to the substituents R′ and *p*-C_6H_4X.

‡ Relative to the substituents R′ and *p*-C_6H_4X.

Table 1. Epoxidation of substituted styrenes and cleavage of the corresponding oxides.

Oxide (alkene)	No.	Acid and solvent	Monoester, % *threo-*	Monoester, % *erythro-*	Reference	Notes
Oxide of *trans*-methylstyrene (XL; R = X = H, R′ = CH_3)	1	H_2SO_4—H_2O	~37	63	82, 83	mixture of diols
	2	CH_3CO_2H	—	80	85	
Oxide of *cis*-methylstyrene (XL; R = X = H, R′ = CH_3	3		90	—	84	
	4		80	~20	82, 83	mixture of diols
(+) and (–) forms of oxide of *trans*-methylstyrene	5	H_2SO_4—H_2O		~76	72	mixture of diols; (–)-*erythro*-glycol is a side-product of the hydrolysis (H_2O–$HClO_4$) (+)-*cis*-oxide.[85]
(+) and (–) forms of the oxide of *cis*-methylstyrene	6		75			
trans-Methylstyrene (XLII; R = X = H, R′ = CH_3)	7	HCO_3H	a	b	82, 83	a small quantity b main product
cis-Methylstyrene (XLIII; R = X = H, R′ = CH_3)	8		b	a		
Oxide of *trans*-stilbene (XL; R = X = H, R′ = C_6H_5)	9	$ClCH_2CO_2H$—C_6H_6	62	—	86	
	10	$ClCH_2CO_2H$—CCl_4	68	—		
	11	Cl_2CHCO_2H—C_6H_6	62	—		
	12	Cl_3CCO_2H—C_6H_6	78	—	87	
(+) and (–) forms of the oxide of *trans*-stilbene	13		71	—		
Oxide of *cis*-stilbene (XLI; R = X = H, R′ = C_6H_5)	14	$ClCH_2CO_2H$—C_6H_6	d	45[c]	86	c isolated in the form of the glycol d traces
	15	Cl_2CHCO_2H—C_6H_6		48		
	16	Cl_3CCO_2H—C_6H_6	—	64	87	
trans-Stilbene (XLII; R = X = H, R′ = C_6H_5)	17	$C_6H_5CO_3H$—Cl_3CCO_2H (1:1) — C_6H_6	72[e]	—		e monotrochloroacetate
cis-Stilbene (XLIII; R = X = H, R′ = C_6H_5)	18		—	44[e]		
Oxide of *trans*-4-methoxystilbene (XL; R = H, X = OCH_3, R′ = C_6H_5)	19	$C_6H_5CO_3H$—$CHCl_3$	70	—	88	
	20	$C_6H_5CO_2H$—C_6H_6	60	—		
trans-4-Methoxystilbene (XLII; R = H, X = OCH_3, R′ = C_6H_5)	21	$C_6H_5CO_3H$—C_6H_6	65	—	89	
	22	$C_6H_5CO_3H$—C_6H_6—H_2O	57	—		
cis-4-Methoxystilbene (XLIII; R = H, X = OCH_3, R′ = C_6H_5)	23	$C_6H_5CO_3H$—$CHCl_3$	43[e]	—	88	f isolated in the form of the glycol
	24		20[f]	76		
Oxide of *trans*-4-methoxy-4′-methylstilbene (XL; R = H, X = OCH_3, R′ = *p*-$C_6H_4CH_3$)	25	$C_6H_5CO_2H$—$CHCl_3$	64	—		
	26	H_2SO_4—H_2O	g			g ratio of diols not stated
trans-4-methoxy-4′-methylstilbene (XLII; R = H, X = OCH_3, R′ = *p*-$C_6H_4CH_3$)	27	$C_6H_5CO_3H$—$CHCl_3$	60	—		
cis-4-Methoxy-4′-methylstilbene (XLIII; R = H, X = OCH_3, R′ = *p*-$C_6H_4CH_3$)	28		—	40		
Oxide of *trans*-α-methylstilbene (XL; R = CH_3, X = H, R′ = C_6H_5)	29	CH_3CO_2H	60	—	66	
	30	Cl_3CCO_2H—C_6H_6	62	—		
	31	mesitylenecarboxylic acid (without solvent)	20	—		
trans-α-methylstilbene (XLII; R = CH_3, X = H, R′ = C_6H_5)	32	CH_3CO_2H	55[h]	—		h isolated in the form of the glycol
	33	$C_6H_5CO_3H$—Cl_3CCO_2H (1:1)—$CHCl_3$	79[i]	—		i monotrichloroacetate

ether, House[97] noted the formation of carbonyl side-products, the quantity of which increases rapidly with increase in the concentration of the complex:



trans -(XLVI) *threo* -(XLVIII) *erythro* -(XLIX) *cis* -(XLVII)

Somewhat unexpectedly there is complete inversion of the configuration in the reaction of a *cis*-epoxypropionamide (XLVII; R = H, R′ = NEt_2) with HCl, both in benzene and in methanol (Table 2, Nos. 14 and 15). Here the *erythro*-isomer (XLIX) is formed. The strict stereospecificity of this reaction is evidently due to the thermodynamic stability of the corresponding transition state, and will be discussed in detail below.

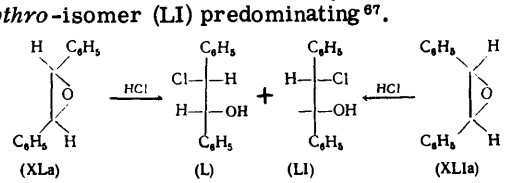
Thermodynamic control probably plays a decisive part in the conversions of some other epoxypropionates. Thus it is well known that acid hydrolysis of *trans*-β-phenylepoxypropionic acid (XLVI; R = H, R′ = OH) proceeds with retention of the configuration and gives *threo*-diol (XLVIII; R = H, R′ = X = OH)[103]. House and Blaker[56] assume the possibility of side reactions for epoxy-β-methyl-β-phenylpropionates (XLVI, XLVII; R = CH_3, R′ = OC_2H_5). However, the available published information on this subject does not permit any general conclusions to be drawn.

Table 2. Halogenohydrins from phenoxides.

Oxide	No.	Reagent and solvent	Yield of halogenohydrin, %		Reference
			threo-	*erythro-*	
Oxide of *trans*-benzalacetophenone (XLVI; R = H, R′ = C_6H_5)	1	HCl—$(C_2H_5)_2O$	43	—	94
	2	HCl—C_2H_5OH	—	44	94,95
	3	$SnCl_4$—C_6H_6	72	—	94,96
	4	0.5 *M* BF_3 $(C_2H_5)_2O$ 2	59	—	
	5	2*M* BF_3 $(C_2H_5)_2O$ 2	38	—	94,97
Oxide of *trans*-dypnone (XLVI; R = CH_3, R′ = C_6H_5)	6	HCl—CH_3CO_2H(HCl—C_2H_5OH)	76	—	98
Oxide of *cis*-dypnone (XLVII; R = CH_3, R′ = C_6H_5)	7		—	84	
trans-Bromodiphenacyl (XLVI; R = CH_2Br, R′ = C_6H_5)	8	CH_3COBr (sealed ampoule, 100°)	58*	—	99, 100
	9		—	60*	
cis-Bromodiphenacyl (XLVII; R = CH_2Br, R′ = C_6H_5)	10	HBr—$(C_2H_5)_2O$—C_6H_6	—	69	100, 101
	11	HBr—$(C_2H_5)_2O$	—	85	100
trans-*NN*-diethyl-3-phenyl epoxypropionamide (XLVI; R = H, R′ = $N(C_2H_5)_2$)	12	HCl—C_6H_6	97	—	102
	13	HCl—CH_3OH	—	94	
cis-*NN*-diethyl-3-phenyl-epoxypropionamide (XLVII; R = H, R′ = $N(C_2H_5)_2$)	14	HCl—C_6H_6	84	—	
	15	HCl—CH_3OH	76	—	
Oxide of *trans*-stilbene (XLa)	16	HCl—C_6H_6	>90	—	67
	17	HCl—$CHCl_3$	>76	—	
	18	HCl—$(C_2H_5)_2O$	75	10	
	19	HCl—dioxan	70	30	
Oxide of *cis*-stilbene (XLIa)	20	HCl—C_6H_6	80	20	
	21	HCl—$CHCl_3$	~80	<10	
	22	HCl—$(C_2H_5)_2O$	87	4	
	23	HCl—dioxan	70	30	

* Acetate of the bromohydrin.

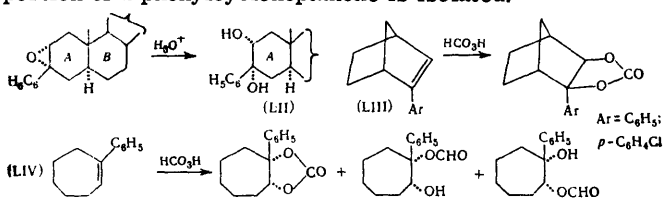
Extremely interesting results were obtained by Berti and coworkers[67] who reexamined previous studies[104-106] of the addition of HCl to isomeric oxides of stilbene (XLa, XLIa). In investigating the effect of solvents of various polarities on the stereochemistry of the reactions, they succeeded in showing (Table 2, Nos. 16–23) that in a comparatively non-polar medium the *trans*-isomer (XLa) undergoes *cis*-opening exclusively, as took place when the same oxide was treated with chloroacetic acids (Table 1, Nos. 9–13). With increase in the polarity of the solvent there is an increase in the yield of the product of the *trans*-opening of the oxide (XLa) and, for example, in the medium of moist ether a mixture of the chlorohydrins is formed with the *erythro*-isomer (LI) predominating[67].



(XLa) (L) (LI) (XLIa)

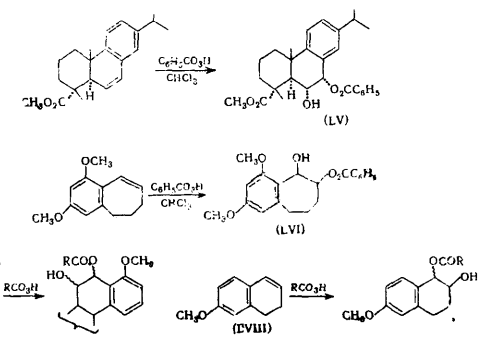
Unlike the *trans*-oxide, the *cis*-isomer (XLIa) in all the solvents used gave mainly the product of *trans*-opening (L) together with small amounts of the diastereoisomer (LI) and carbonyl compounds. These results differe from those in which there is exclusively *cis*-opening of oxide (XLIa) under the action of chloroacetic acids (Table 1, Nos. 14–16), which could be due to the nature of the carboxylate and halide nucleophilic ions, which participate in the realisation of the corresponding transition states[67].

The epoxides of aryl cyclenes stand somewhat apart from the aryl oxides considered above. There is extremely little information on their *cis*-opening, just as for the *cis*-addition of the elements of per-acids to the corresponding alkenes. It is known, for example, that acid hydrolysis of 2α,3α-epoxy-3β-phenylchloestane gives only the 2α,3α-glycol (LII)[107]. A similar result is obtained in the epoxidation with performic acid of the arylnorbornenes (LIII)[108,109] and phenylcycloheptene (LIV).[110] In the latter instances, in addition to the orthocarbonate and a mixture of monoformates (the secondary formate arises as a result of the migration of the formyl group) a considerable proportion of a phenylcycloheptanone is isolated.



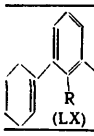
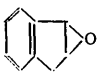
Only keto-products are formed in the epoxidation of Δ⁶-dehydroabietane by perbenzoic acid[111]. For the same reason the yield of the *cis*-benzoate (LV) from methyl Δ⁶-dehydroabietate is only 43%.[111]

On the basis of the spectroscopic results and analogies in the literature, the sole product of the epoxidation of dimethoxybenzocycloheptadiene was ascribed the structure of the *cis*-monobenzoate (LVI).[112] More frequently, however, examples are encountered when arylcyclenes and their oxides give mixtures of substances which are epimeric at a benzyl centre. Thus, the addition of the elements of per-acids to the steroidal fragment (LVII), used by Johnson and coworkers[113,114] in the synthesis of aldosterone proceeds non-selectively and gives a mixture of monoesters of isomeric diols. A similar picture is observed in the epoxidation of methoxydihydronaphthalene (LVIII)[73,74] and in the conversions of the oxides and alkenes (LIX)–(LXII) shown in Table 3.



The data given in Table 3, while not so complete as for the acyclic aryl oxides considered above, nevertheless permits the conclusion that the opening, which is catalysed by acids, of the phenylcyclohexene oxide (LIX) and indene oxide (LXI) in polar media takes place with considerable inversion of the initial configuration. This conclusion is confirmed by the results on the opening of oxide (LIX) by an aqueous solution of sodium nitrite in acetic acid[126] and also by the preliminary results of Berti and coworkers[127] in respect of the influence of polar and ionising strength of the medium on the direction of the opening of phenylcyclohexene oxides. In investigating, in particular, the

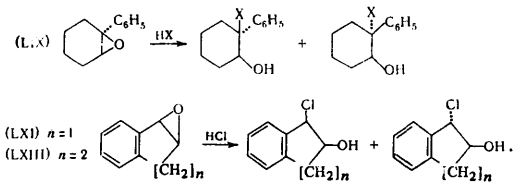
Table 3. Cleavage of cyclic aryl oxides and epoxidation of arylcyclenes.

Oxide (alkene)	No.	Reagent and solvent	Yield of glycol, % cis-	Yield of glycol, % trans-	Reference
(LIX)	1	H_2O	51	—	115, 116
	2	H_2O—H_2SO_4	42—60	21—50	58, 117—120
	3	HCO_2H—$(C_2H_5)_2O$	90	10	59
	4	Cl_3CCO_2H—C_6H_6	65[a]	—	
 (LX) R=R'=H	5	HCO_3H	67—95	0—5	59, 108, 121
R=CH_3; R'=H	6	CH_3CO_3H	50	—	121
R=R'=OCH_3	7	HCO_3H	70	—	122, 123
 (LXI)	8	H_2O	38	19	58
	9	H_2O—$NaHSO_3$	60	20	124
	10	H_2O—H_2SO_4	41	—	58
	11	H_2O—CH_3CO_2H	50	19	
	12	H_2O—$FClO_3$— — dioxan	48	48	125
(LXII)	13	HCO_3H	35[b]	5[b]	68

[a] Secondary trichloroacetate. [b] 2-Formate.

acid hydrolysis in various media, including such strongly ionising solvents as dimethyl sulphoxide (DMSO) and hexamethylphosphoric triamide (HMTA), Italian investigators[127] found that the percentage retention of the configuration of these oxides falls rapidly in the following sequence of solvents: $C_6H_6 > HCO_2H > H_2O >$ dioxan + $H_2O >$ DMSO + $H_2O >$ HMTA + H_2O.

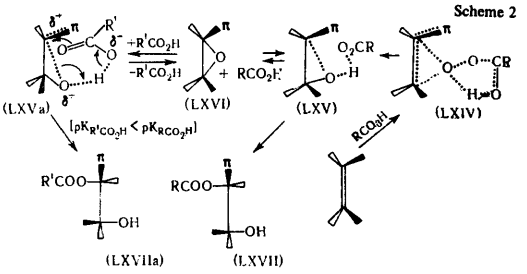
The meagre available information suggests that the above regularity is also observed in the opening of aryl oxides by hydrogen halides[128-130]. Thus, in the treatment of the oxide (LIX) with hydrogen chloride or bromide in the relatively non-polar chloroform, only the product of *cis*-opening is produced, whereas in alcoholic medium a mixture of halogenohydrins epimeric at a benzyl centre is formed[128]. A mixture of *cis*- and *trans*-isomers is also produced in the reaction of hydrogen chloride with indene oxide (LXI) and dihydronaphthalene oxide (LXIII) in dioxan[129]:



The above influence of the polarity of the medium on the direction and stereochemistry of the opening of cyclic aryl oxides should probably appear in the epoxidation of arylcyclenes. The published information confirms this suggestion. In fact, in a comparatively non-polar medium the process proceeds with a high degree of selectivity, giving products of the *cis*-addition of the elements of the per-acids at a double bond (Table 3, Nos. 5–7, 13). Here it must be noted that both in the epoxidation of phenylcyclohexene by performic acid and in the opening of epoxide (LIX) with formic and trichloroacetic acids (Table 3, Nos. 3 and 4) an increase in the yield of the *trans*-compounds on reducing the reaction temperature is observed[59]. As for the influence of conformational factors on the direction and stereochemistry of the opening of cyclic arylepoxides, except for a preliminary report[127] on the opening of the conformationally fixed phenylcyclohexene oxides, there is hardly any published information on this subject at present.

2. Mechanism of the *cis*-opening of aryl oxides. An examination of the material shows that analogous final results are obtained irrespective of whether one is dealing with the addition of per-acids to aromatic alkenes or with the opening of the corresponding oxides under conditions of electrophilic catalysis. In the general form this can be expressed by Scheme 2.

Scheme 2



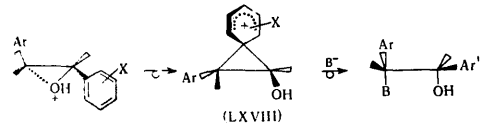
It is well known that the epoxidation of alkenes is an irreversible process, which is evidently not subject to the action of acid catalysis[6,89,131,132] and probably proceeds through the formation of a spiran[133] transition state (LXIV). The geometry of the latter is evidently not symmetrical[134,135] and reflects both the state of the electron density of the double bond being attacked (determined, in turn, by the nature of the substituent) and also by the nature of the attacking electrophilic reagent. Such a view of the nature of the transition state (LXIV) is purely speculative but it finds indirect confirmation in the kinetic results for the oxidation of a series of alkenes by per-acids. For example, whereas, according to Lynch and Pausacker[132] and Campbell and coworkers[89], if the rate of oxidation of *trans*-stilbene (XLII; R = X = H; R' = C_6H_5) by perbenzoic acid (benzene, 25°C) is taken as unity, then the ratios of the oxidation rates of the corresponding 4-Cl-, 4-CH_3O-, and 4-CH_3O-4'CH_3O-substituted compounds under the same conditions is approximately 0.6 : 5 : 20. Similar results were obtained by Ogata and Tabushi[134,135] in the epoxidation of certain α-methylstilbenes. It also follows from the kinetic results that the irreversible decomposition of the transition state (LXIV) should lead to the formation of the protonated oxide (LXV). The latter, in its turn, is in equilibrium with a carboxylic acid produced from the per-acid and with the epoxide (LXVI), which is the final product of the reaction on using per-acids of the monoperphthalic type. The existence of such an equilibrium was convincingly demonstrated by experiments on the oxidation of *trans*-4-methoxystilbene with perbenzoic acid containing labelled benzoic acid[89]. It appeared from this that the formation of the final benzoate is equally probable from both the labelled $C_6H_5CO_2H$ initially present in the substrate and the $C_6H_5CO_2H$ produced from the perbenzoic acid. The oxidation of stilbene by perbenzoic acid in the presence of trichloroacetic acid, as a result of which trichloroacetates (but not benzoates) of hydrobenzoins (Table 1, Nos. 17, 18, 33) are obtained also shows the probability of the existence of an intermediate oxide (LXVI) in view of the impossibility of the exchange reaction[89,136]:

$$RCO_3H + R'CO_2H \rightleftarrows RCO_2H + R'CO_3H.$$

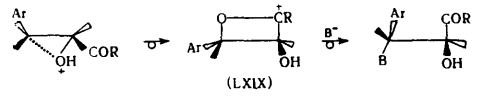
Furthermore, experiments with mixtures of acids clearly demonstrate the well known fact that the opening of an epoxide ring is catalysed by acid; therefore in the presence of two acids of unequal strength the conversion of the oxide (LXVI) into the final products (LXVII, LXVIIa) proceeds more rapidly with the stronger acid.

Consequently, both the addition of the elements of the per-acid to an aromatic alkene, and the acid-catalysable opening of the corresponding oxide proceeds through an intermediate protonated epoxide (LXV, LXVa), the conversion of which is a kinetically controllable stage of both processes[89,132]. Thanks to the appearance of a dynamic effect of conjugation, the protonated oxide, which, like transition state (LXIV), probably cannot be symmetric, is characterised by the presence of a broken C–O bond and consequently a rather stable carbonium ion in the vicinity of the electron-donating substituent[65,128,134,135].

To explain the formation of products of the *cis*-opening of aryl oxides several schemes have been proposed. According to one of these, a double inversion with participation of the "phenonium" ion (LXVIII),[88] or of a four-membered oxide ring (LXIX),[98] is assumed to be possible in systems of the stilbene oxide or dypnone oxide type:

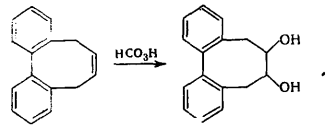


(LXVIII)



(LXIX)

These schemes have been criticised repeatedly[87,92,110], although decisive arguments against them have not been forthcoming. However, such hypotheses can explain only a few particular examples and in several other instances the formation of a "phenonium" ion is improbable (for example, phenylpropene, indene, etc.). Furthermore, it must be noted that the formation of a four-membered transition state, in particular (LXIX), is energetically unfavourable[137]. Nevertheless, the recently described *cis*-addition of the elements of performic acid to dibenzocyclooctatriene (LXX)[138] can be regarded as the result of the stabilisation of the corresponding transition state by a mechanism of the "phenonium" ion type:

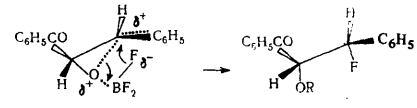


(LXX)

In fact, both reaction centres of the original alkene are homobenzylic and for such systems a transition state of type (XXXVI) cannot be represented.

According to the scheme which seems most probable at present, the *cis*-opening of the oxide ring is described by a "push-pull" process taking place in the "solvent cage".[92] Here the state of the mutual orientation of the C–O bond of the epoxide and the molecule of proton-donating nucleophilic reagent is considered. The molecules of the epoxy-compound and of the proton donor, being included in the "solvent cage", interact with one another in the way typical of hydrogen bond formation[3,6,98]. The "pulling" force here is the progressing protonation of the oxidic oxygen atom. As a result of this protonation there is a removal of the stress in the three-membered ring and the formation of a stabilised carbonium ion, together constituting the driving force of formation of a transition state of type (LXV). Because the elements of the "ion pair"[92,98] are favourably arranged in this way at the side of the nucleophilic reagent, a minimal "push" is required for converting the transition state (LXV) into the final product (LXVII) with the configuration of the initial oxide (LXVI). Here the role of the steric factors, which hinder the approach of the nucleophilic reagent, are probably insignificant.

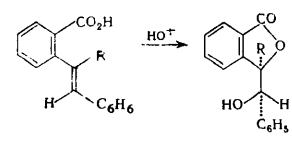
The "phenonium" ion and "ion pair" schemes have been widespread in the literature and there has recently been a worthy attempt to combine them[67]. However, the scheme involving the "ion pair" is preferred more often as it allows a large number of experimental facts to be explained. For example, by starting from these hypotheses the *cis*-opening of epoxides under the action of a Lewis acid can be described by a scheme which House[139] proposed when he obtained the *cis*-fluorohydrin on treating *trans*-benzalacetophenone oxide with boron trifluoride–diethyl ether:



where R = BF_2 or H.

An analogous succession of changes occurs apparently in the reaction of stilbene oxides with phenylmercaptoborane[79] and hexadeuteriodiborane[140].

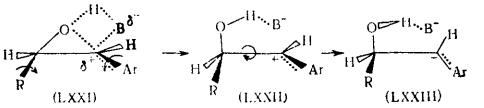
The idea of the orientated complex of the epoxide and the proton-donating nucleophilic reagent allow the influence of the solvent on the occurrence of the "sterically anomalous" opening of the oxide ring to be explained. In fact it is easy to suggest that the formation of this complex, considering the nature of the forces acting, which was discussed above, will be more probable in a non-polar (non-ionising) solvent. On the other hand, in an ionising solvent its destruction will be more probable. Therefore a greater percentage of configuration retention is to be expected in non-polar systems, which agrees with the results shown in Tables 1–3. Furthermore, in a polar (non-ionising) solvent the degree of dissociation of the acidic nucleophilic reagents considered in the tables is increased. This indicates that there is a simultaneous increase in both the number of protonated (and more solvated) epoxide molecules of the (XXXVI; A = H^+) type and the concentration of strongly nucleophilic ions RCO_2^- and X^-. Hence conditions are created for the attack of the oxide ring from any side and the probability of an energetically favourable bimolecular *trans*-opening increases. An analogous situation is observed when a nucleophilic reagent is fixed by the structure of the molecule itself so that attack with formation of inverted products is always possible, as occurs in the opening of the isomeric 2-stilbazole oxides[141] and the epoxidation of stilbene-2-carboxylic acids[142–144]. In these instances, irrespective of the polarity of the medium, *trans*-opening of the epoxide ring is observed exclusively, for example:



where R = H, CH_3.

This scheme explains the reduced stereospecificity observable during the opening of the *cis*-aryl epoxides (Tables

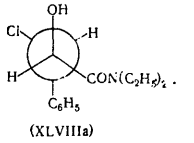
1 and 2), in which the "*cis*-effect"[145] of neighbouring bulky groups appears. This effect should facilitate the conversion of the transition state (LXXI) of the *cis*-aryl oxide into its extreme state (LXXII) with sp^2-hybridised benzyl carbon atom. For the same reason rotation of the plane of this centre around the C–C bond by 90° is possible before attack by the nucleophilic ion B^- takes place.



(LXXI) (LXXII) (LXXIII)

As a result of the isomerisation[67] of cisoid cation (LXXII) into the stable transoid one through intermediate state (LXXIII), a product should arise with inverted configuration of the initial oxide and such an explanation of its formation seems better founded than direct *trans*-addition of the nucleophilic reagent. The probability of the isomerisation should increase on using a polar solvent, just as it should on increasing the steric capacity of the neighbouring substituents (increase in the "*cis*-effect"). Tables 1 and 2 confirm this assumption. We can take as an example the epoxidation of the 4-methoxystilbenes by perbenzoic acid: from the *trans*-isomer only the *threo*-monobenzoate is obtained, whereas the *cis*-isomer gives a mixture of diastereoisomers (Table 1, Nos. 21–24). Analogous results are obtained in the opening of the stilbene oxide by hydrogen chloride (Table 2, Nos. 16–23). The observed preferential formation of reaction products with retention of the configuration of the *cis*-isomer does not agree with the behaviour of the same oxide in relation to chloroacetic acids, where there is *cis*-opening (Table 1, Nos. 14–16). Berti and coworkers[67] explain this difference by the reduced nucleophilic nature of the chloride ion in comparison with carboxylate ions, which attack the cisoid intermediate state of type (LXXII) before its isomerisation takes place. The results of Tung and Speziale on the opening of the *cis*-epoxypropionamide by hydrogen chloride (Table 2, Nos. 14 and 15) can be explained similarly,

Probably the already rather weak protonation of the oxide ring for the interaction between the two hindered bulky groups in the transition state (LXXI; R = $CONEt_2$, Ar = C_6H_5, B = Cl) led to the energetically more favourable state of type (LXXIII), the subsequent neutralisation of which gives the *threo*-chlorohydrin (XLVIIIa):

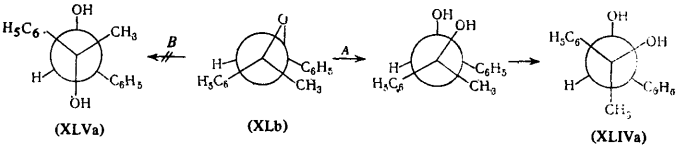


(XLVIIIa)

There is also the noteworthy fact that in the treatment of the *threo*-chlorohydrin (XLVIIIa) with sodium methoxide in addition to the expected *cis*-epoxypropionamide (XLVII; R = H, R′ = NEt_2) the *trans*-isomer (XLVI; R = H, R′ = NEt_2) is obtained, in the ratio 3 : 2. On the other hand, the *erythro*-chlorohydrin (XLIX; R = H, R′ = NEt_2, X = Cl) under these conditions is converted quantitatively into the *trans*-epoxypropionamide[102].

So far we have discussed examples which illustrate the dependence of the *cis*-opening of the oxide ring on the polarity of the solvent, on the nucleophilic nature of the reagent, and also on the steric factors which influence the formation of the transition state, leading to this type of result. It was noted above, however, that the secondary-tertiary α-methylstilbene oxide undergoes *cis*-opening irrespective of the polarity of the solvent (Table 1, Nos. 29–31). An analysis of the results in Table 2 allows a similar steric selectivity to be found for secondary-tertiary bromodiphenacyls and dypnone oxides.

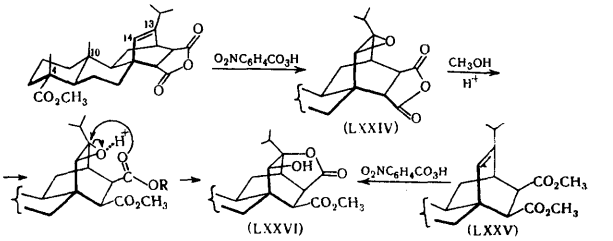
Purely qualitative consideration of the acid hydrolysis of *trans*-α-methylstilbene oxide (XLb) which takes place with breaking of the tertiary C–O bond[66] suggests with a high degree of probability that here also the predominating influence is the steric factor, which determines the formation of the energetically most favourable transition state. In fact, path *B*, as a result of which the *erythro*-diol (XLVa) should be formed, corresponding to the *trans*-opening of the initial oxide, requires the surmounting of a considerable energetic barrier in the transition state, due to the interaction of hindered methyl and phenyl groups.



(XLVa) (XLb) (XLIVa)

On the other hand, for the realisation of the transition state from which the experimentally observable *threo*-diol (XLIVa), with the configuration of the initial oxide, is obtained, the surmounting of a minimal energetic barrier is necessary (path *A*). It is easy to see that analogous considerations can lead to identical conclusions for the secondary-tertiary dypnone oxide and halogenodiphenacyl oxides. Unfortunately, a more rigorous discussion of these energetic factors is impossible owing to lack of quantitative data.

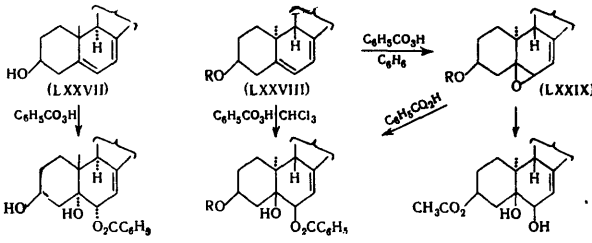
The influence of the steric factor on the direction of the acid-catalysed opening of an epoxide ring can be illustrated by the methanolysis of oxide (LXXIV) obtained from the adduct of methyl laevopimarate with maleic anhydride, and also the epoxidation of the unsaturated diester (LXXV)[146]. The *cis*-hydroxylactone (LXXVI) which is liberated in both instances with a yield of ~ 45% is evidently formed by intramolecular attack on the protonated epoxide by the solvated carboxyl group. Intermolecular attack of the nucleophilic reagent, leading to products of *trans*-opening, is probably hindered by screening of the $C_{(13)}$–$C_{(14)}$ bond by the axial methyl groups at $C_{(4)}$ and $C_{(10)}$. The examples examined show the possibility in principle in some instances of the *cis*-opening of epoxide in systems which differ from oxides of the (XXXV) type.



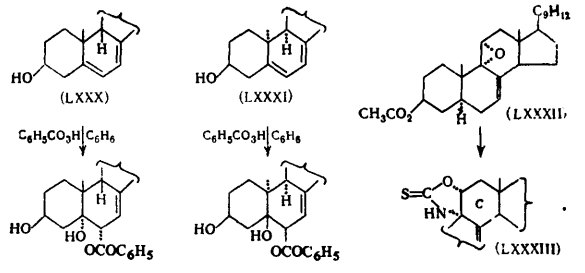
(LXXIV) (LXXVI) (LXXV)

3. *cis*-Opening of mono-oxides of conjugated dienes and of oxides of enol-esters. The *cis*-opening of monoxides of conjugated dienes was observed mainly in the steroid series. In every instance in discussing the reaction mechanism the stable allyl carbonium ion is considered, nucleophilic attack of which should be effected from the sterically least hindered region of the steroidal molecule. In fact, on treating ergosterol (LXXVII) with perbenzoic acid only the 5α,6α-glycol benzoate is formed[147]. On the other hand the conversion of

lumisterol (LXXVIII), which exhibits "unfavourable" combination of rings A, B, and C, leads exclusively to the 5β,6β-diol monobenzoate[148-150]:



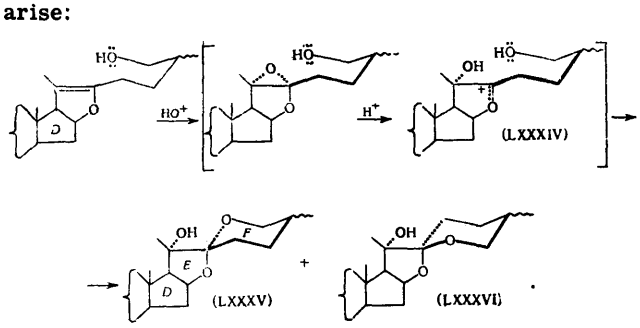
The opening by benzoic acid and water[148-150] of lumisterol β-oxide (LXXIX) obtained by oxidation of the diene (LXXVIII) in benzene[149,150] proceeds in an analogous manner. The epoxidation of 9β-ergosterol (LXXX) and of 9α-lumisterol (LXXXI) by perbenzoic acid in benzene is also accompanied by the formation of considerable quantities of the products of the *cis*-opening of the corresponding unstable allyl epoxides. The authors[151] think that the latter are intermediates in both reactions:



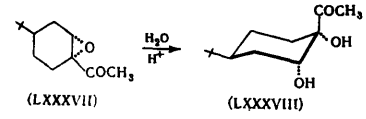
Mention must also be made of the result obtained by Ueda and Mosettig[152], who observed the *cis*-opening of ergostadiene 9α,11α-oxide (LXXXII) into the thio-oxazolidone (LXXXIII) in the presence of hydrogen thiocyanate.

Apart from what has been considered above there is hardly any published information on the "sterically anomalous" opening of other monoxides of conjugated dienes. Reference can only be made to results on the epoxidation of cyclopentadiene by peracetic[153] and performic[154] acids and the hydrolysis of the corresponding monoepoxides[155]. In every instance a complex mixture of products is obtained, among which *cis*-cyclopentene-1,2-diol is observed.

In the steroidal series several instances have been described of the stabilisation of the carbonium ion produced during epoxidation by the unshared pair of *p*-electrons of a neighbouring oxygen atom. Thus, in the treatment of pseudosapogenions with per-acids the kinetically controllable rear attack of the OH group of the side-chain of the stabilised carbonium ion (LXXXIV) can lead to the formation of products of *cis*-opening (LXXXV) of the intermediate oxide[156,157]. In the presence of destabilising thermodynamic factors[157] *trans*-opening products (LXXXVI) also arise:

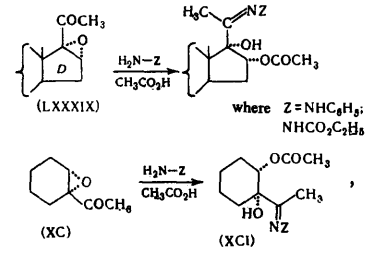


4. *cis*-Opening of oxides of conjugated ketones. Information has recently been published on the *cis*-opening of αβ-epoxyketones of the cyclohexane and steroid series under conditions of acid catalysis. The main distinguishing characteristic of these conversions is evidently the fact that in every instance, as will be shown below, the C–O bond in the α position to the keto-group of the initial epoxide is broken. This signifies the appearance in the corresponding transition state of a deficiency in the electron density adjacent to the carbonyl function. By virtue of the electron-withdrawing nature of the latter such a state should exhibit high energy[158,159]; however, there is the possibility of its being reduced, owing to enolisation of the C=O group[160]. Here the transition state will be represented by the special case of the states of type (XXXVI) considered above, and probably in acid hydrolysis of the keto-oxide (LXXXVII) it is partly realised with formation of the *cis*-diol (LXXXVIII)[161].



This example is still the only one in the keto-oxide series, analysis of the conversions of which is often hindered by the possible formation of secondary products as a result of enolisation, retroaldolisation, epimerisation, etc. taking place. All the remaining known instances of *cis*-opening relate to the reactions of keto-oxides in the presence of reagents at the carbonyl group.

Such a reaction was first described in the patent literature[162] as a method for obtaining substituted 16α,17α-glycols from pregnane 20-keto-16α,17α-epoxides (LXXXIX) in the presence of phenylhydrazine. The latter was soon replaced by ethoxycarbonylhydrazine (ECH)[163]. Subsequently it was shown by the example of acetylcyclohexene oxide (XC) that products with retained configuration (XCI) are also formed in the presence of semicarbazide, 2,4-dinitrophenylhydrazine, and hydroxylamine[164]

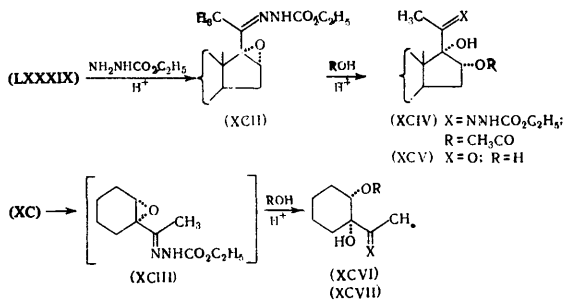


where Z = $NHCO_2C_2H_5$, $NHCONH_2$, $NHC_6H_3(NO_2)_2$, or OH.

As a result of a thorough study of the reactions of steroidal keto-oxides (LXXXIX) with ECH it was found that the opening of the epoxide ring precedes the formation of the corresponding carbonyl derivatives (XCII)[69,165,166], and in some instances the process almost stops at this stage[167,168]. An analogous sequence of changes is also observed in the cyclohexane series, although for the keto-oxide (XC) the intermediate ethoxycarbonylhydrazone (XCIII) could not be isolated[164].

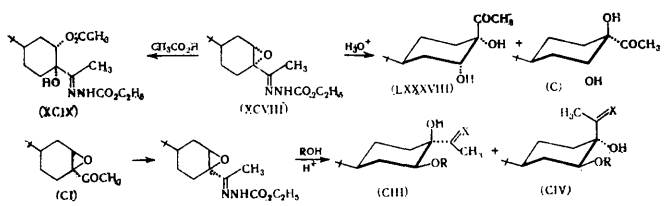
A detailed analysis of the way in which these reactions proceeded showed that the stages of "sterically anomalous" hydrolysis of the hydrazone-oxides (XCII) and (XCIII) and the removal of the hydrazone grouping from compounds of

the type (XCIV) and (XCVI) can coincide, which was verified in practice.



Hence the keto-oxides (LXXXIX) and (XC) could be converted, formally in one stage, into the corresponding *cis*-keto-glycols (XCV) and (XCVII)[169,170] and a synthesis of the latter in the steroidal series by this path is probably the simplest and most reliable[171].

Interesting results were obtained in investigating similar changes of the conformationally fixed stereoisomeric keto-oxides (LXXXVII) and (CI)[172,173]. In the presence of ECH they are also converted into ethoxycarbonylhydrazones (XCVIII) and (CII), the acetolysis of the α-isomer being strictly stereo-directed, leading exclusively to the secondary acetate (XCIX):



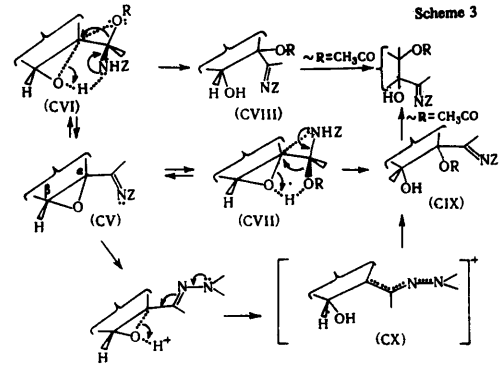
where X = O, $NNHCO_2C_2H_5$; R = H, CH_3CO.

The acid hydrolysis of the α-hydrazono-oxide (XCVIII) proceeds less selectively and gives a mixture of keto-glycols (LXXXVIII) and (C) in the ratio ~ 3 : 2. In acetolysis and hydrolysis of the β-isomer (CII) such selectivity in the opening of the oxide ring is not observed. However, in these instances in the mixture of products (CIII) and (CIV), the *trans*-diequatorial isomer (CIV) predominates. This emphasises the fact that as a result of the acetolysis of the ethoxycarbonylhydrazones of the oxides secondary acetates are isolated in all the examples examined.

The acid hydrolysis of the ditertiary oxide of 1-acetyl-2-methylcyclohex-1-ene in the presence of ECH gives a mixture of diastereoisomeric keto-glycols[168]. In this respect the results obtained are analogous to those given above for the conversion of keto-oxides (LXXXVII) and (CI) under the same conditions. However, with the conformationally labile ditertiary keto-epoxide an analysis of the results is hindered by the observed isomerisation of the product of the *cis*-opening of the oxide into the *trans*-glycol[168].

The available results, in particular those on the opening of the keto-oxides (XCVIII) and (CII) allow us to speak about the structural directionality of the conversions. Namely, in every instance the introduction of a molecule of water or acetic acid takes place at the carbon centre of the epoxide adjacent to the hydrazone group. The formation of secondary acetates of keto-diols is the consequence of the instability of the initially formed tertiary esters, which then undergo intramolecular reesterification[70,71]. These results show the presence of an electron-deficient α carbon atom of the hydrazono-oxide in its opening. The possibility of attack at this centre by molecules of nucleophilic reagents is shown in Scheme 3.

Scheme 3



According to Scheme 3, under the reaction conditions the carbonyl derivative (CV) is in equilibrium with the isomeric carbinolamines (CVI) and (CVII). As a result of the intramolecular attack of the residue OR situated in the immediate vicinity of the reaction centre keto-glycols and their derivatives (CVIII) and (CIX) are formed. Here it is considered[69,166] that the stabilisation of the electron-deficient α carbon centre in the transition states (CVI) and (CVII) is effected by the unshared p-pair of electrons of the oxygen and nitrogen atoms respectively. On the whole this scheme is similar to the "ion pair" scheme considered above.

However, it was shown that the keto-oxides (LXXXVII), (XC), and (CI) do not undergo opening on replacing the reagents for the carbonyl group by primary amines of various basicities[172-174]. This fact suggests the participation in the redistribution of the electron density of the second nitrogen atom of the hydrazine derivatives, or of the oxygen atom of the hydroxylamine derivatives. The protonation of the oxygen atom of the epoxide leads to the formation of transition state (CX) which is characterised by the presence of a positive charge on the α carbon atom, stabilised by $p\pi$-conjugation. Furthermore, it cannot be ruled out that stabilisation is effected by the unshared p-pair of electrons of the imine nitrogen atom of the hydrazonium group. The subsequent attack of this centre by the nucleophilic reagent can lead to products with either retention or inversion of the configuration of the original keto-oxide.

It should be noted that the schemes discussed allow these transformations to be considered as formally similar in mechanism to the reduction of a keto-oxide in the presence of chromium(II) salts[175,176], by the method of Huang-Minlon[177], by the method of Wharton and Bohlen[178], and also to conversions of α-substituted ketones in the presence of hydrazine derivatives[179-182]. At present it is quite difficult to choose between the schemes for the conversion of the carbonyl derivatives of cyclic $\alpha\beta$-epoxy-ketones that we have considered. In these systems, just as in a series of aryl oxides, the decisive role is evidently played by the nucleophilic nature of the reagent, the polarity of the medium, and also the steric and conformational factors.

---oOo---

The material considered on the "sterically anomalous" opening of an epoxide ring allows the conclusion that reactions leading to the formation of products with retention of the configuration of the initial oxide include the act of

interaction of the nucleophilic reagent with the deficit in electron density arising on one of the carbon centres of the epoxide ring in the transition state. The solvated carbonium ion intermediate is usually stabilised by π- or p-electrons adjacent to the epoxide ring grouping. The formation of products with retention of the configuration of the original epoxy-compound depends on the direction of nucleophilic attack, which is determined by the steric effects of the addition of the nucleophilic reagent to the carbon atom carrying a stabilised positive charge. In this discussion the term "sterically anomalous" opening of the oxide ring acquires formal significance.

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Polymerisation of Lactones

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This is a review of investigations on the polymerisation of lactones. The author briefly touches on the history of the subject, the advantage of the synthesis of polyesters by the method of polymerisation over polycondensation, and the essential nomenclature of lactones. The polymerisation of β-, γ-, and δ-lactones, both unsubstituted and with various substituents, in the presence of anionic and cationic catalysts, and also under the action of ionising radiation, is considered in detail. Conditions and possible schemes of mechanism for the polymerisation of these lactones, and also the effect of substituents on the course of the process, are given. Examples of the copolymerisation of this class of compounds with either vinyl or cyclic monomers are considered separately. The available published data on the physicochemical properties of polyesters synthesised from lactones and their applications as fibre- or film-forming polymers is presented. Bibliography of 80 references.

CONTENTS

I. Introduction 463
II. Polymerisation of β-lactones 463
III. Polymerisation of γ- and δ-lactones 466
IV. Copolymerisation of lactones 467

I. INTRODUCTION

The first communications on the polymerisation of lactones date from 1903, when Fichter and Beisswenger[1] and later Hollo[2] obtained from liquid monomeric δ-valerolactone a waxy crystalline mass, m.p. 47–48°C. Carothers and coworkers[3] showed that a mixture of oligomers with $M = 3000–4000$ is formed.

Great attention is now being paid to the polymerisation of oxygen-containing cyclic esters, especially lactones. The formation of polyesters in this manner has considerable advantages over polycondensation. Firstly, the process can be carried out under milder conditions, at negative or near-room temperatures; secondly, the need for removing side-products disappears, which is not true for polycondensation. These advantages enable polyesters of high molecular weight which exhibit a series of valuable physicochemical properties and are suitable for the preparation of high-quality fibres and films to be obtained.

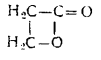
Lactones are polymerised in the presence of acid and basic catalysts, complex catalysts, and under the action of ionising radiations. They are not polymerised by a radical mechanism.

There is some confusion in the literature concerning the terminology of lactones. Usually the name of a lactone is derived from the name of the acid on the basis of which it is constructed, but some authors name the lactone by starting from the total number of carbon atoms entering into the lactone, and others, from the number of carbon atoms forming the lactone ring. We think that the second principle of classification is the more rigorous and subsequently will adhere to the following nomenclature: four-membered lactone, β-propiolactone; five-membered γ-butyrolactone; six-membered, δ-valerolactone; seven-membered, ε-caprolactone. The positions of the substituents at carbon atoms of the lactone ring will be shown by starting the numbering from the carbonyl-carbon.

II. POLYMERISATION OF β-LACTONES

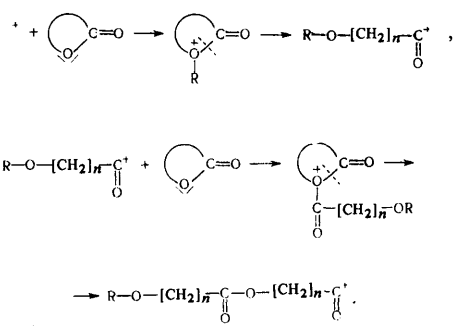
1. Unsubstituted β-Lactones

One of the most studied representatives of the class of lactones is β-propiolactone:



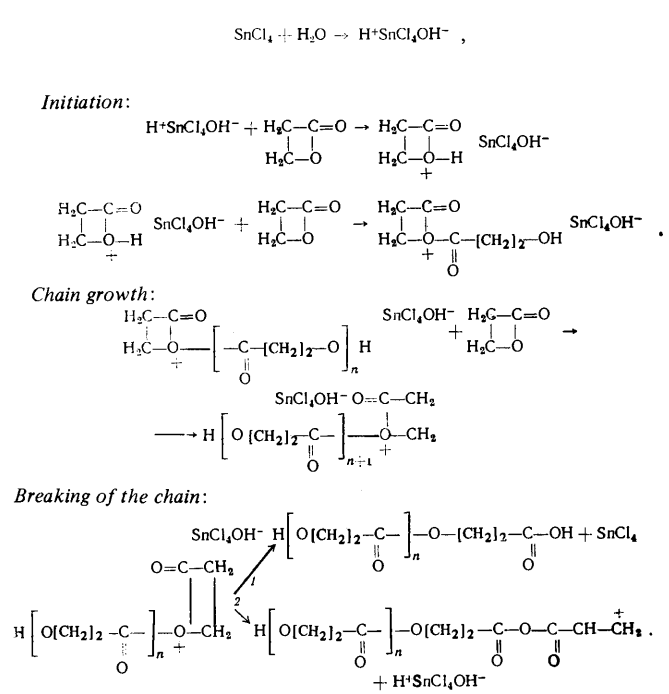
The reactions of β-propiolactone with various organic and inorganic compounds were investigated in detail by Gresham and coworkers[4–15].

Cationic polarisation. In 1948 Gresham and coworkers[6] first described the formation of a polymer with $M = 800–1000$ in the reaction of β-propiolactone with conc. H_2SO_4 or $FeCl_3$. In 1962, Cherdron and coworkers[17] investigated the polymerisation of β-propiolactone in the presence of $AlCl_3$ and acetyl perchlorate. The initial β-propiolactone was distilled in thoroughly dried apparatus under a vacuum in the presence of 2% tolylene di-isocyanate. The purity of the product was checked by gas chromatography and from the stability of the monomer on storage (at a temperature $\gtrsim$ 60°C). The polymerisation was carried out at 20°C without solvent under an atmosphere of nitrogen in the presence of the above catalysts, in 1×10^{-3} M concentration. The polymers obtained had a polyester structure with $M \simeq 100\,000$. The following mechanism was proposed for the cationic polymerisation of lactones:



Yamashita and coworkers[18] carried out the polymerisation of β-propiolactone in the presence of conc. H_2SO_4 and also Lewis acids ($FeCl_3$, $SnCl_4$, $AlCl_3$, $ZnCl_2$, and BF_3. ether) at 0° and 20°C for a long time (24 h to 5 months). Low-molecular weight polymers were obtained ($\eta_{sp}/c = 0.05$) with m.p. 76–80°C. Polymers are not formed in the presence of $ZnCl_2$ and $HgCl_2$. On the basis of the infrared

spectra and the terminal groups of the polymers the following mechanism of polymerisation in the presence of the $SnCl_4$–H_2O system was proposed:



The first mechanism of chain rupture mainly prevails, but at elevated temperatures the second reaction is also possible. In another study [19] Yamashita states that the principal reason for the breaking of the chain is the presence in the reaction system of negligible amounts of water. Recently, patents [20,21] and a paper [22] have appeared dealing with the polymerisation of β-propiolactone in the presence of Ti, Zr, and V phosphates. The polymers obtained had $[\eta]$ from 1 to 5.

Anionic Polymerisation. There have been more studies of the anionic polymerisation of β-propiolactone than of its cationic polymerisation. This is due to the principal possibility of carrying out the process in the presence of a series of catalytic systems without breaking of the chain and this in turn leads to the preparation of polymers with a higher molecular weight.

Gresham and coworkers [16] were the first to find that a low-molecular-weight product is formed by the action of NaOH on β-propiolactone, In continuing the work on the polymerisation of cyclic esters, Furukawa and coworkers [23,24] tested a series of organometallic compounds as catalysts for the polymerisation of β-propiolactone. These compounds are used both in the pure state and with cocatalysts. Low-molecular-weight polymers with $[\eta] < 0.2$ were synthesised.

Unlike the Japanese investigators, Cherdron and coworkers [25] found that thoroughly purified β-propiolactone in the presence of anionic catalysts gives high-molecular-weight polymers even at room temperature. Under the action of sodionaphthalene in dioxan solution at 100°C a polymer with $[\eta] \simeq 3$ is formed, but on polymerisation in the presence of aluminium alkyls products with M = 70 000–100 000 are obtained without cocatalysts. Use of water as cocatalyst leads to a considerable increase in the molecular weight of the polyester in accordance with the ratio of aluminium alkyl (or halogenoalkylaluminium) to water.

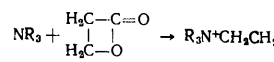
In their discussion of the mechanism of the anionic polymerisation the authors consider that, just as in the cationic process, the opening of the lactone ring takes place at the acyl bond, at which a negative charge passes from the initiator to the oxygen atom of the ring, which then reacts with a new molecule of the monomer.

Japanese investigators [18,19,22,26–28] tested a large number of inorganic and organic compounds of basic nature as catalysts for the polymerisation of β-propiolactone (Table 1). Of the compounds examined, the most effective catalysts are betaine, pyridine, and pyridine derivatives. Kagiya and coworkers [27,29] studied the polymerisation of β-propiolactone in the presence of pyridine and tried to relate the process determining the rate of reaction, the molecular weights, and the yield of polymers to the concentrations of the monomer and catalyst, the temperature, and the polymerisation time. The variation of the rate of the process with the ratio of monomer to catalyst is expressed by a curve with a maximum. On carrying out the reaction in a solvent, the activity of the catalyst increases with the dielectric strength of the medium and the monomer concentration. The scheme of the process is analogous to that of anionic polymerisation proposed earlier [25], with the addition of possible variants in the chain breaking and transfer.

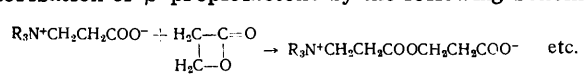
Table 1. Polymerisation of β-propiolactone in the presence of various anionic catalysts.

Catalyst, class of compound, and example	Conditions of reaction			Yield, %	η	Reference
	Temp., °C	Time, h	concn. of catalyst, mole per mole monomer			
Metal hydroxides (calcium, potassium, barium)	0—80	1—360	10^{-2}	70—90	0.1—0.5	22,26,28
Salts (potassium, sodium, or rubidium carbonates, etc.)	30	72—600	0.5—$2\cdot10^{-2}$	20—70	0.4	22,26,28
Alkoxides (sodium ethoxide, magnesium isopropoxide)	15	1000	0.3—$3\cdot10^{-3}$	50—70	0.4—0.6	19
Organic bases (triethylamine, betaine, pyridine, alkaloids)	0—25	200—800	$4\cdot10^{-3}$	70—90	0.5—1	19,22,27

In 1963 Etienne and Soulas [30] reported that in the presence of betaine β-propiolactone forms polymers of high molecular weight. It was noted earlier [31–33] that betaine or betaine-like complexes are formed by the action of tertiary amines on β-propiolactone:



which under appropriate conditions then leads to the polymerisation of β-propiolactone by the following scheme:



The authors of this scheme consider that the best catalyst of this type is the compound obtained in the reaction of a lactone and a tertiary amine; however, ordinary betaine (the internal salt of hydroxycarboxymethyltrimethylammonium or glycine trimethylbetaine) and glycine benzyldimethylbetaine are only slightly inferior. In the presence of these catalysts at a concentration of 0.1 mole % for 8–10 h at 15–20°C polymers of β-propiolactone with $[\eta] = 1.5$ were obtained. There is also a series of patents on the

polymerisation of β-propiolactone under the influence of organic compounds of the metals of Periodic Groups I and III,[34,35] alkalis on cotton wool[36] or wool[37], salts of Group I metals, and weak inorganic acids[38].

Polymerisation under the action of ionising radiations. Okamura and coworkers investigated the polymerisation of β-propiolactone under the action of γ-rays in the solid state[39-41] and in solution[42] at −78° and −196°C. Large and small crystals of β-propiolactone were irradiated (power of dose 10^3–10^6 roentgen h^{-1}). The products of highest molecular weight are formed from coarse crystals, hence the growth of the polymeric chain proceeds in a direction perpendicular to the long axis of the crystal monomer, and hence with increase in the size of the crystal the molecular weight of the polymer rises. At −78°C a crystalline polymer is formed even on irradiating fine crystals, but at −196°C an amorphous polymer is obtained. On the basis of X-ray investigations[39] and electron microscopy[40] it is suggested that the act of initiation takes place at the junctions of crystals and especially at places of crystal lattice defects. The yield of poly-β-propiolactam does not exceed 15–20%, $[\eta] = 0.15$–0.2, m.p. 110–120°C. In these studies the effect of post-polymerisation after cessation of the irradiation of the specimen is noted. The yield and viscosity of the polymer rise with increase in the dose power[43]. An anionic mechanism is proposed for the polymerisation of β-propiolactone under the action of γ-rays.

Apart from γ-irradiation, visible light in the presence of uranyl nitrate as an activator of the reaction[44], ultraviolet radiation[45], and beams of electrons with dose power 1.6×10^{-4}–20 Mrad min^{-1} [46] are also used for the initiation of the polymerisation of β-propiolactone, but only in the last instance could a polymer with $[\eta] = 1.4$–2.56 be isolated, though in very low yield. In the other instances low-molecular weight products were obtained in low yield.

Structure and properties of poly-β-propiolactone. Elemental analysis of the synthesised polymers and of the products of their acid and alkaline hydrolysis[18,26], chemical analysis of the terminal groups[17,18,25,47], infrared spectra[18,22,26,27,47,48] and the results of differential thermal analysis[22] show that the poly-β-propiolactone has the structure of a complex polyester, however, in connection with the absence of a common opinion about the site of the opening of the lactone ring during polymerisation there is still no definite conclusion concerning the regularity of the alternation of the links in the chain of the macromolecule. It is found, however, that the structure of the polyester obtained from the lactone differs from that of the polyester obtained in the polycondensation of diols and dicarboxylic acids[25].

In studying the infrared spectra of polymer films two types of structure were observed, the formation of which depends on the polymerisation conditions, particularly the nature of the catalyst[28]. However, the polymers of different structure did not exhibit differences in chemical properties and there were no differences in the infrared spectra of solutions of these polymers. The possibility of polymorphism of these polymers was suggested[47]. The existence of different crystal structures of poly-β-propiolactone was confirmed by Furukawa's investigations and also by Kagiya and coworkers[22]. Crystalline poly-β-propiolactone was obtained, which contained α and β forms with crystallisation temperatures of 65° and 20°C respectively and differed in X-ray diagrams and infrared spectra. It was found that the α form, with a repeat unit of 7.02 Å, has a 2_1 helical structure, whereas the β form, with repeat unit 4.28, has a planar zig-zag structure. The β form can be converted into the α by slow heating of a film of the polymer to 65°C. The β form is formed when the film is obtained from chloroform solution by slow evaporation; after rapid evaporation the α form predominates.

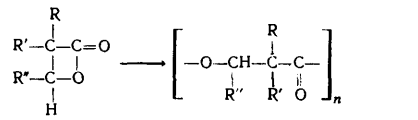
Similar investigations were made by Gianalvise[49], who determined, from the X-ray patterns of powders and fibres of poly-β-propiolactone, the repeat unit (6.02 Å) and also the unit-cell parameters and proposed the most probable helical structure of the macromolecule and its packing.

Poly-β-propiolactone is a mainly crystalline product with decomposition temperature 80–122°C and density from 1.2 to 1.4 (depending on the molecular weight). It is soluble in several organic solvents. According to the differential thermal analysis[22], the decomposition temperature of the polymer lies within the limits 230–250°C, but these values can be raised by increase in the molecular weight of the polymer. Owing to its low softening temperature poly-β-propiolactone is used as a modifier in natural fibres[36,37] or is mixed with other polymers which are more stable on heating.

2. Alkyl-Substituted β-Lactones

A patent[50] which appeared in 1960, and an article by the same authors[51] in 1962, described the production of polymers of a series of substituted β-propiolactones in the presence of triethylamine or triethylenediamine in bulk and in solution at 80–100°C. Some of the polymers obtained have high melting points (Table 2), and the lactones with a more symmetrical structure gave polymers with a higher molecular weight and which were more crystalline.

Table 2. Melting points of polymers of alkyl-substituted β-propiolactones.



Substituent			Melting point, °C
R	R′	R″	
CH_3	CH_3	H	240
CH_3	C_2H_5	H	125
CH_3	n-C_3H_7	H	80
CH_3	iso-C_3H_7	H	2[illegible]
CH_3	n-C_4H_9	H	liquid
CH_3	n-C_5H_{11}	H	54
C_2H_5	C_2H_5	H	226—245
C_2H_5	n-C_3H_7	H	200—205
C_2H_5	n-C_4H_9	H	179—180
n-C_3H_7	n-C_3H_7	H	257
n-C_3H_7	n-C_4H_9	H	227
n-C_4H_9	n-C_4H_9	H	245
—$[CH_2]_5$—		H	260—270
CH_3	CH_3	CH_3	185
CH_3	CH_3	C_2H_5	150

Most of the polymers synthesised are soluble in chlorine-containing solvents and form flexible transparent films which have a higher hydrolytic stability, and are more resistant to the action of HBr, dilute alkalis, and hydrazine solution than the polyesters obtained by polycondensation.

The polymerisation of $\alpha\alpha\beta$-trisubstituted lactones in the presence of betaine [30] is analogous to the polymerisation of the unsubstituted lactone [30], and the presence of alkyl substituents in the α position facilitates attack of the carbonyl carbon of the ring at the COO^- side of the anion and accelerates the polymerisation.

Yamashita and coworkers [18,26] carried out the polymerisation of α-methyl-, β-methyl, $\beta\beta$-dimethyl-, and β-isopropyl-β-propiolactones in the presence of anionic and cationic catalysts. All the polymers synthesised had low molecular weights ($[\eta] = 0.03-0.1$). The following series of activities of the β-propiolactones was compiled on the basis of the size of the molecular weight and the polymerisation times. In polymerisation in the presence of acid catalysts: $\beta\beta$-dimethyl > unsubstituted > α-methyl $\geq$ $\geq$ β-methyl > β-isopropyl; for basic catalysts: unsubstituted > α-methyl $\geq$ β-methyl > β-isopropyl > > $\beta\beta$-dimethyl. The polymerisation of $\alpha\alpha$-dimethyl-β-propiolactone [19] and $\beta\beta$-dimethyl-β-propiolactone [52] was investigated in greater detail. In the polymerisation of the former in the presence of CH_3CO_2K or KOH at 50°C high-molecular weight ($[\eta] = 1.7-2.6$) polymers, m.p. 230–240°C, were obtained in ~ 100% yield. The polymers are soluble in phenol, cresol, and trichloroacetic acid at elevated temperature. It was found that increasing the polymerisation time and also the $[M]/[C]$ ratio facilitates an increase in the degree of polymerisation. It was suggested that under these conditions "living polymers" are formed. In the polymerisation of $\alpha\alpha$-dimethyl-β-propiolactone in the presence of acid catalysts at 100°C only low-molecular-weight products are obtained. For the polymerisation of $\beta\beta$-dimethyl-β-propiolactone in the presence of $SbCl_5$, $SnCl_4$, and $ZnCl_2$ at 0°C polymers with $[\eta] = 0.08-0.12$ are formed after several days in yields of ~ 30%. When $Al(C_2H_5)_3$ or $Al(C_2H_5)_3-H_2O$ are used as catalysts under the same conditions polymers with a higher molecular weight ($[\eta] = 0.2-0.37$) are formed; however, in comparison with unsubstituted β-propiolactone and $\alpha\alpha$-dimethyl-β-propiolactone the activity of the β-substituted lactone during polymerisation is less. The reduction of activity is explained [52] firstly by the instability of the monomer itself at elevated temperature ($\beta\beta$-dimethyl-β-propiolactone readily decomposes into isobutene and CO_2), and secondly by the presence of a chain-transfer reaction, especially in the presence of cationic catalysts.

Interesting work on the determination of the activity of α-substituted β-propiolactones during polymerisation in the presence of basic catalysts, particularly pyridine, was begun by a group of Japanese investigators [53], who calculated, on the basis of the C–C "skeleton method" the delocalisation energy of the electrons in the lactone ring and also the frontal distribution of electron density as a function of the nature of the substituents at the carbon atoms of the lactone ring. Starting from the calculated values of the coulombic and resonance integrals, schemes of the frontal distribution of electron densities were drawn up for four types of α-substituted β-propiolactones and the following series of their polymerisation rates in decreasing order (substituents shown) given: $\alpha\alpha$-bis(chloromethyl) > α-chloromethyl-α-ethyl > α-chloromethyl-α-methyl > unsubstituted > $\alpha\alpha$-dimethyl.

3. Halogeno-substituted β-Lactones

Only a few papers have been published on the polymerisation of halogeno-substituted β-propiolactones and these deal only with the polymerisation conditions and certain properties of the polymers obtained. Thus in the polymerisation of $\alpha\alpha$-bischloromethyl-β-propiolactone [54] in the presence of powdered KOH for 6 h at 40–50°C a polymer with decomposition temperature ~ 300°C is obtained, from which fibres can be spun which exhibit a capability for cold drawing. On heating this monomer at 100–120°C for 5 h a polymer was obtained [55] with m.p. ~ 300°C, insoluble in most organic solvents and thermally stable at 230–250°C. A polymer of $\alpha\alpha$-bischloromethyl-β-propiolactone was obtained in the presence of KOH, triethylamine, and pyridine at 50°C. [56] Under these conditions $\beta\beta$-bischloromethyl-β-propiolactone was polymerised only in the presence of acid catalysts ($AlCl_3$, $SnCl_4$, BF_3.ether) and the above basic catalysts were ineffective [56]. The melting point of the polymer of $\beta\beta$-bischloromethyl-β-propiolactone is 150–160°C. Apart from the chloromethyl derivatives of β-propiolactone mention has been made of the production of polymers from $\alpha\alpha$-bisbromomethyl-, $\alpha\alpha$-bisfluoromethyl-, and α-bromomethyl-α-ethyl-β-propiolactones in the presence of triethylamine or triethylenediamine [51].

III. POLYMERISATION OF γ- AND δ-LACTONES

Nothing has been published on the production of homopolymers from γ-lactones, and only two papers have been published about the copolymerisation of γ-butyrolactone, which will be discussed below.

Six-membered or δ-valerolactones easily form polymers in the presence of ionic catalysts, sometimes even more easily [17,25] than β-lactones and polymers were first synthesised from lactones on the basis of δ-valerolactone [1,2]. Carothers and coworkers [3] obtained poly-δ-valerolactone with $M = \sim 4000$ by heating the monomer at 150°C in the presence of K_2CO_3 for 5 h. The polymers were waxy products with m.p. 53–55°C. Cherdron and coworkers [17,25] not only studied the polymerisation of β-propiolactone but also investigated the polymerisation of δ-valerolactone and ϵ-caprolactone. They proposed a mechanism of cationic and anionic polymerisation of these lactones analogous to the mechanism of cationic and anionic polymerisation of β-propiolactone with breaking of the acyl bond of the ring, in which the anionic mechanism differed from that proposed earlier by Stannett and Szwarc [57]. On the basis of a comparison of polymerisation rates and molecular weights of the polymers the following series of activities was found for the three lactones: ϵ-caprolactone > δ-valerolactone $\geq$ $\geq$ β-propiolactone, and from ϵ-caprolactone and δ-valerolactones polymers with $M \simeq 100\,000$ were obtained.

Satome and Hadira [58] effected the polymerisation of δ-valerolactone in the presence of ethyleneglycol and ethanolamine for 10 h at 100–180°C. Since the molecular weight of the polymers obtained did not exceed 2000 and the melting point was < 50°C, the course of the process was followed by the change in the refractive index n_D^{50} of the reaction mixture. The molecular weight of the polymer formed increased linearly with the ratio $[M]/[C]$; water in the system at a concentration < 0.01% had no significant effect on the rate of the process but catalytic additions of H_2SO_4, $AlCl_3$, or Na accelerated the reaction, their activity falling in the sequence H_2SO_4 > $AlCl_3$ > Na. The activation energy of the process was 6.4 kcal $mole^{-1}$. The suggested mechanism of initiation and growth of the polymeric chain is analogous to that proposed earlier [17]. On esterification of the synthesised polymer at the terminal OH groups a polyester thermostable at 200°C (it did not lose weight on heating at 200°C for 6 h) was obtained.

Several patents dealing with the polymerisation of ϵ-caprolactones in the presence of chelates of the Group IV metals of the Periodic System and of acylates of fatty acids[59]; a series of alkoxides of Sn, Pb, and Mn[60]; mineral acids and Lewis acids[61]; alcohols, amines, and amino-alcohols[62]; alkoxides of Na, K, Li; $LiAlH_4$; $NaBH_4$;[63] organometallic compounds of Periodic Group I, II, and III;[64,65] borates and oxides of Zn and Pb; and organotitanium compounds[66] have been published. The molecular weights of polymers described in the patents listed varied in a wide range from 900 to 250 000. These polymers are recommended to be used for obtaining fillers, coatings, lacquers, films, and fibres, and mixed with other polymers[67,68], for the preparation of various plastics.

IV. COPOLYMERISATION OF LACTONES

With the aim of increasing the thermal stability and of simultaneously retaining the valuable properties of lactone polymers, studies were undertaken on the copolymerisation of a series of lactones with vinyl or other cyclic monomers. The greatest number of papers deals with the copolymerisation of β-propiolactone and the second component most frequently used is a cyclic ether. The copolymerisation of β-propiolactone with 3,3-bischloromethyloxacyclobutane (BCCB)[69-67] in the presence of BF_3.ether and of the $Al(C_2H_5)_3-H_2O$ system at $-50°$ and 0°C has been described. On the basis of the elemental analysis and infrared spectra it has been found that both components react and form a copolymer, which consists of chloroform-soluble and chloroform-insoluble fractions, with m.p. ~ 125° and ~ 160°C respectively. BCCB is a more active monomer both in cationic and in anionic copolymerisation. Alkaline hydrolysis shows the block structure of this copolymer. Furukawa and coworkers[72] carried out the copolymerisation of β-propiolactone with tetrahydrofuran, epichlorohydrin, and ethylene oxide in the presence of the same catalysts at 0°C. Tetrahydrofuran and especially epichlorohydrin form with β-propiolactone in the presence of $Al(C_2H_5)_3-H_2O$ almost alternating copolymers. In using BF_3.ether copolymers are obtained only with tetrahydrofuran ($r_1 = 2.9$, $r_2 = 0.4$). Propylene oxide does not undergo copolymerisation with β-propiolactone.

An interesting attempt to obtain a copolymer of β-propiolactone with γ-butyrolactone was made by Furukawa and coworkers[73], who carried out the copolymerisation of these monomers in the presence of $Al(C_2H_5)_3-H_2O$, $Zn(C_2H_5)_2-H_2O$, $Al(iso\text{-}C_3H_7O)_3$, KOH, and K_2CO_3 at 0° and 25°C in the bulk and in solution (toluene, methylene chloride). The copolymer of β-propiolactone with γ-butyrolactone is formed only in the presence of the catalytic system $Al(C_2H_5)_3-H_2O$. From the constant activity of the monomers ($r_1 = 18 \pm 2$, $r_2 = 0.36 \pm 0.1$) it was concluded that γ-butyrolactone enters into the composition of the copolymer to an insignificant amount in the form of blocks with not more than two or three units of γ-butyrolactone.

The possibility of the copolymerisation of β-propiolactone with vinyl compounds was also studied. In the reaction[74] of acrylonitrile with β-propiolactone in the presence of such organometallic compounds as $SrZn(C_2H_5)_4$, $Al(C_2H_5)_3$, sodium naphthenate, and systems of C_4H_9Li with $Al(C_2H_5)_3$, $B(C_4H_9)_3$, $Cd(C_2H_5)_2$ at room temperature a mixture of chloroform-soluble and chloroform-insoluble products was formed. The soluble fraction consisted of a homopolymer of β-propiolactone and the insoluble contained a homopolymer of acrylonitrile and its copolymer with β-propiolactone. However, the yield of copolymer was insignificant and the rate of reaction low.

The grafting of β-propiolactone to the copolymer of acrylonitrile and diketen has been described[75]. The addition of β-propiolactone here proceeded owing to the opening of the diketen ring in the copolymer, that is, the diketen served as a transition link between the vinyl and the cyclic compound, uniting two types of polymerisation. Therefore a direct relation was observed between the diketen concentration in the copolymer of it with acrylonitrile and the quantity of graft β-propiolactone.

In the radical copolymerisation[76] of styrene with β-propiolactone in the ratio 85 : 15 a block copolymer with terminal OH and COOH groups is formed correspondingly. Block copolymers of styrene and β-propiolactone are also obtained in cationic copolymerisation ($SnCl_4$, 0°C, in toluene)[77].

In an attempt to obtain copolymers of β-propiolactone with propylene sulphide in the presence of $(C_2H_5)_3N$ and also with the *N*-carboxy-anhydride of DL-valine in the presence of pyridine it was found that in the first instance copolymerisation does not take place and in the second a compolymer with $M \simeq 1200$ is formed, with the copolymerisation constant showing low activity of the β-propiolactone[78].

The copolymerisation of β-propiolactone, γ-butyrolactone, and ϵ-caprolactone with ethyleneimine has been investigated[79]. The copolymerisation was carried out in the presence of $SnCl_4$, BF_3.ether, $(C_2H_5)_3N$, NaCN, and $HgCl_2$, in various solvents with dielectric constants from 2.38 to 37.6 at temperatures of $-35-0$°C, 35–100°C, and 100°C, for the β-, γ-, and ϵ-lactones respectively. Low-molecular-weight products were obtained. The yield of copolymers increases with increase in the dielectric constant of the solvent. On the basis of a comparison of the infrared spectra of the products synthesised and of model compounds containing the elementary unit of the polymer, five different structures were proposed according to the site of the opening of the lactone ring. Two structures are formed owing to the breaking of the Alk-O bond in the β-propiolactone in solvents with a high dielectric constant. In a medium with a low dielectric constant ring opening takes place at the acyl bond in all the lactones listed, independently of the medium.

Yamashita and coworkers described the copolymerisation of $\beta\beta$-dimethyl-β-propiolactone with 3,3-bischloromethyloxacyclobutane[52] and with styrene[77]. In addition, they investigated the copolymerisation of 3,3-bischloromethyloxacyclobutane with unsubstituted β-propiolactone, α-methyl-, β-methyl-, $\alpha\alpha$-dimethyl-, $\beta\beta$-dimethyl-, and β-isopropyl-β-propiolactone, which was carried out in the presence of BF_3.ether at 0°C. The greatest activity in cationic copolymerisation is exhibited by $\beta\beta$-dimethyl-β-propiolactone. It is thought that the mechanism of the ring opening of this monomer differs from the others because the two methyl groups at the β-carbon atom, owing to a redistribution of the electron density of the ring, facilitate breaking of the Alk–O bond with the formation of a tertiary carbonium ion. In the remaining investigations of lactones under the selected conditions ring opening takes place at the acyl–O bond. The following series of activities of these lactones in cationic copolymerisation with 3,3-bischloromethyloxacyclobutane was obtained: $\beta\beta$-dimethyl- $\gg$ $\gg$ β-methyl > unsubstituted $\geqslant$ α-methyl > $\alpha\alpha$-dimethyl. The activity of lactones in copolymerisation increases with increase in the number of alkyl substituents at the β-carbon atom, owing to an increase in the nucleophilic nature of the ester oxygen of the lactone ring. However, this value in β-lactones is low in comparison with simple cyclic esters, which is particularly clear on comparing the values

of the copolymerisation constants. Thus for the most active ββ-dimethyl-β-propiolactone $r = 1.42 \pm 0.1$ but for 3,3-bischloromethyloxacyclobutane $r = 7.24 \pm 0.32$. The reason for the comparatively low activity of β-lactones is thought to be the low nucleophilic nature of the ester oxygen owing to the drawing off of the electrons by the adjacent carbonyl group. A general tendency was noted for a decrease in the activity of β-lactones on the introduction of alkyl substituents in the α-position in anionic polymerisation and an increase in activity on the introduction of alkyl substituents in the β-position in cationic polymerisation, which is correspondingly reflected in the properties of the polymers.

Higher lactones, for example, γ-butyrolactone and ε-caprolactone give copolymers with ethyleneimine[79], as mentioned above, and also with 3,3-bischloromethyloxacyclobutane and β-propiolactone[80]. In the last instance the copolymerisation was carried out in the presence of BF_3.ether at room temperature or at 0°C. These lactones form copolymers with 3,3-bischloromethyloxacyclobutane, the activity in the copolymerisation of the lactones being in the following order: ε-caprolactone > γ-butyrolactone > > β-propiolactone. On the basis of the copolymerisation constants it was found that the activity of ε-caprolactone is higher than that of 3,3-bischloromethyloxacyclobutane but that of γ-butyrolactone is somewhat less. In the copolymerisation of β-propiolactone products of comparatively low molecular weight ($[\eta] = 0.06-0.25$) are obtained.

On the basis of the studies reviewed it can be concluded that lactones are of interest both for studying polymerisation processes connected with ring-opening and as prospective raw materials for obtaining polyesters which exhibit several valuable properties.

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Gas Hydrates

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This review states contemporary views about gas hydrates, and also about non-stoichiometric clathrates with the general formula $M.nH_2O$. The known types of the hydrates and their crystal structure are described. The thermodynamics of hydrate formation is considered. Methods of determining the composition of the hydrates are described. Factual information concerning the hydrates of individual gases and organic liquids and mixed hydrates (binary and multicomponent) is given. The problem of the stabilisation of hydrates by an auxiliary gas is considered. Information is given about the density of hydrate crystals and the physical kinetics of the hydrate formation. Equations are given which are obtained by the methods of statistical mechanics and are based on the use of Lennard-Jones and Kihara potentials, and allow the main thermodynamic properties of the hydrates to be calculated. The problems of the industrial utilisation of the hydrates are examined (desalination of sea water, separation of liquid and gaseous mixtures, etc.). The theoretical principles of the inhibition of hydrate formation processes are stated. Bibliography of 180 references.

CONTENTS

I. Introduction 469
II. Contemporary views about gas hydrates 470
III. Conditions for the formation of hydrates 471
IV. Methods of preparation and of determining the composition of hydrates 472
V. Thermodynamics of hydrate formation 473
VI. Stabilisation of hydrates with the aid of an "auxiliary gas" 474
VII. Hydrates of individual gases and volatile organic liquids 474
VIII. Mixed hydrates 480
IX. Calculation of the conditions of hydrate formation and of the compositions of the solid (hydrate) and gas phases 484
X. Use of the principles of statistical mechanics in studying gas hydrates. 486
XI. Physical kinetics of the formation of hydrates. 487
XII. Density of hydrate crystals 487
XIII. Industrial use of gas hydrates 488
XIV. Prevention of hydrate formation 488

I. INTRODUCTION

Gas hydrates are solid crystalline substances with the appearance of snow or loose ice and the general formula $M.nH_2O$, where M is the hydrate-forming molecule. There is considerable theoretical interest in the investigation of gas hydrates, as they allow general laws to be formulated which describe the unique physical properties of an extensive group of clathrate compounds† in which the crystal

† Contemporary views about gas hydrates as non-stoichiometric clathrates are presented in Chapter II of this review.

lattice is constructed from water molecules but nevertheless differs appreciably from the lattice of ordinary ice (stability at temperatures > 0°C, presence of cavities of strictly determined diameter, etc.).

Practical interest in gas hydrates is connected with the following features. A series of processes which are carried out in the oil, gas, and petrochemical industries is accompanied by the formation of hydrocarbon hydrates which clog pipelines and equipment. To prevent hydrate formation it is necessary to know the conditions of formation of the hydrates for various compositions of the gas phase, temperatures, pressures, and other parameters, which determine this process. Three prospective directions for the industrial use of gas hydrates must also be noted: (1) the desalination of sea water (semi-industrial plants are already known to be in operation); (2) the separation of binary and multicomponent gas and liquid mixtures; (3) the storage of gases.

Davy[1] first obtained a gas hydrate of chlorine in 1811 on cooling a saturated aqueous solution of chlorine at 9°C. In the first half of the XIXth century hydrates of Br_2, SO_2, and H_2S were obtained in this way.

Thanks to the work of Cailletet, Vroblevskii, Villard, de Forcrand, and other investigators[1] in the 1850s to 1890s, the hydrates formed by CO_2, CS_2, C_2H_2, PH_3, AsH_3, CH_4, C_2H_6, C_2H_4, C_3H_8, N_2O, Ar, Kr, and Xe became known.

A large group of so-called "double hydrates"‡ was then studied, formed by H_2S or H_2Se with hydrocarbons and their halogen derivatives (predominantly of the aliphatic series): CH_3Cl, C_2H_5Br, C_2H_5I, etc. and also hydrates formed by the mixtures: $CO_2 + PH_3$, $CS_2 + PH_3$, $C_2H_2 + CCl_4$, and hydrates obtained from halogen-substituted aliphatic hydrocarbons and such compounds as C_2H_4, CO_2, SO_2, and others.

In the first third of the XXth century the investigation of gas hydrates was mainly connected with the defining of the conditions for the formation of previously known hydrates and of obtaining some new hydrates (CF_4, CHF_3, SO_2Cl_2, I_2, etc.)[1-3]. There was an appreciable increase in interest in studying gas hydrates after the publication of Hammerschmidt's first work[4], who showed in a study of the hydrates of individual C_1–C_4 aliphatic hydrocarbons, that the serious difficulties arising in the transport of natural gas were connected with the formation in the pipelines of the so-called "mixed hydrates". During these years there appeared a great number of papers devoted to defining the equilibrium conditions for the formation of hydrates by individual hydrocarbons, their mixtures, the composition of the hydrates, and methods of preventing hydrate formation. All these problems have been covered completely enough in Frost and Deaton's monograph[5]. As a result of the fundamental investigations made by Stackelberg[6-18], Claussen[19,20], and also Pauling and Marsch[21], in the 1950s the structure of the hydrate crystals was determined, the ideas about "mixed hydrates" were significantly extended, the stabilising influence of foreign gases was studied, and the thermodynamics of hydrate formation and other problems were considered.

At the end of the 1950s and start of the sixties theoretical studies devoted to the statistical mechanics of gas hydrates appeared[22-29]. Between 1960 and 1966 the existence of hydrates of oxygen and nitrogen at high pressures was shown experimentally[30,31] and the theoretical investigations were pursued further[32-37].

‡ As will be shown below, "double hydrates" are particular examples of "mixed hydrates".

II. CONTEMPORARY VIEWS ABOUT GAS HYDRATES

Current literature[38] devoted to the structure of gas hydrates recognises the viewpoint first expressed by Nikitin[39-43]. According to this viewpoint, gas hydrates (formed by individual gases or their mixtures) are non-stoichiometric inclusion compounds, "gas clathrates"[28,44,45], in which the "included" molecules of gas are held by van der Waals forces in a metastable crystal lattice, the "host", which is constructed from water molecules.

The investigations of Claussen[19,20], Pauling and Marsch[21], Stackelberg and Müller[8,9], and Mandelcorn[46] have shown conclusively that gas hydrates crystallise in one of two cubic structures, (I) or (II), the interaction between the water molecules from which the lattice is constructed being effected by means of hydrogen bonds.

The hydrates of structure (I) are described by space group $Oh^3 = Pm3n$ and are characterised by the crystal lattice parameter 12 Å. The unit cell is constructed from 46 water molecules and in it there are eight cavities available for gas molecules, including 2 "small" cavities and six "large". The "small" cavities of structure (I) are regular pentagonal dodecahedra with mean free diameter ~ 5.1 Å; each of the six "large" cavities is tetrahedral with a mean free diameter of ~ 5.8 Å, formed by two opposing hexagons and 12 pentagons situated between them.

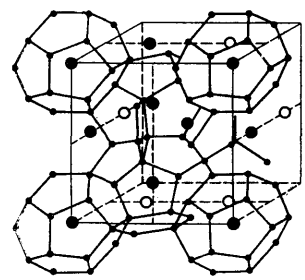

Figure 1. Crystal lattice of a gas hydrate of structure (I).

The hydrates of structure (II) are described by space group $Oh^7 = Fd3n$ with crystal lattice parameter 17.4 Å. The unit cell is constructed from 136 water molecules, contains 24 cavities, including 16 "small" and 8 "large". The "small" cavities, as for structure (I), are pentagonal dodecahedra, but somewhat deformed, as a result of which the mean free diameter is ~ 5 Å. The "large" cavities of structure (II) are hexadecahedra, each of which is constructed from four hexagons and 12 pentagons. The mean free diameter of this cavity is ~ 6.7 Å.

When the effective diameter of the hydrate-forming molecule ($d_{eff}^{M_1}$) < 5.1 Å, then a hydrate of structure (I) is formed in the presence of water; in principle, all the eight cavities can be filled (hydrates of Ar, CH_4, H_2S, etc.) and consequently the ideal formula of this hydrate will be $8M_1.46H_2O$ or $M_1.5.75H_2O$, where M_1 can be a molecule of Ar, CH_4, H_2S, etc. When 5.8 Å > $d_{eff}^{M_2}$ > 5.1 Å, then the hydrate-forming molecules can fill only the six large cavities: in this instance the ideal formula of the hydrate will be $6M_2.46H_2O$ or $M_2.7\frac{2}{3}H_2O$ ($M_2 = C_2H_6$, Cl_2, SO_2, etc.). When two types of molecule are present simultaneously in the gas mixture (a mixture of $M_1 + M_2$) a so-called "mixed hydrate" with the ideal formula $2M_1.6M_2.46H_2O$ is formed, which can

be considered as a solid solution[28,40-42] with a composition which changes during fusion of the hydrate. An example of a "mixed hydrate" of structure (I) is $2H_2S.6C_2H_6.46H_2O$.

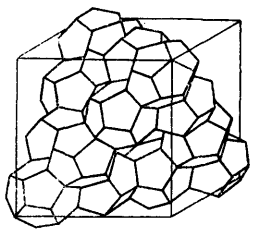

Figure 2. Crystal lattice of a gas hydrate of structure (II).

Analogous considerations apply for a hydrate of structure (II). When 5 Å $< d_{\text{eff}}^{M_3} <$ 6.7 Å (C_3H_8, iso-C_4H_{10}, $CHCl_3$, etc.), then the ideal formula of the hydrate will be $8M_3.136H_2O$ or $M_3.17H_2O$. For the mixture $M_3 + M_4$ (under the conditions: $d_{\text{eff}}^{M_4} < 5$ Å), the "mixed hydrate" which is formed is characterised by the ideal formula $16M_4.8M_3.136H_2O$ or $2M_4.M_3.17H_2O$; for example, $2H_2S.C_3H_8.17H_2O$ or $2CH_4.C_3H_8.17H_2O$.

Figs. 1 and 2 show schematically hydrates of structures (I) and (II).

III. CONDITIONS FOR THE FORMATION OF HYDRATES

A clear presentation of the conditions of formation of hydrates according to the equation $M + nH_2O \rightleftharpoons M.nH_2O$ can be obtained by considering the diagram of heterogeneous equilibrium in P–t coordinates proposed by Roozeboom[47] and given in one of Stackelberg's papers[10]. On this diagram (Fig. 3): (a) curve *I* characterises the saturation vapour pressure of the hydrate-forming substance P_M which in its turn is saturated with water vapour; (b) curve *II*, the vapour pressure of the hydrate-forming substance M over the hydrate in the presence of liquid water; (c) curve *II′* is the vapour pressure of M over the hydrate in the presence of ice; (d) curve *III* is the variation of the melting point of the hydrate with the pressure; (e) curve *IV* is the depression of the freezing point of water during the dissolution of M in it under pressure.

As Fig. 3 shows, the region of existence of hydrates is situated to the left of curves *II* and *III*. The intersection of these curves gives the so-called "critical point for the decomposition of the hydrate" P_c, which is simultaneously the upper quadruple point of the system; at this point hydrate + M_{gas} + M_{liq} + water coexist. It should be noted that point P_c is absent from the hydrates formed by such gases as Ar, CH_4, C_2H_4, Kr, Xe, N_2, and O_2, since owing to the low values of the critical temperature, curve *I* for these gases falls below curve *II* up to the intersection point. The intersection of curves *II′* and *II* gives the so-called "lower quadruple point" at which hydrate + ice + water + M_{gas} coexist. When the pressure in the system is below P_c, then on heating the hydrate decomposes into water and gas (on crossing curve *II*).

When the pressure in the system exceeds P_c, then on raising the temperature (passage through curve *III*) the hydrate decomposes into two liquid phases, H_2O and M_{liquid}.

Curve *III* itself characterises the P–t_f dependence for condensed systems. For the hydrates this curve is almost vertical. The slope of the curve to left or right ($dt/dp < 0$ or $dt/dp > 0$) will depend on how much the volume of the solid hydrate is greater or less than that of the liquid phase which is formed in the fusion of the hydrate§. From the equation given above for the formation of a hydrate comes the idea of dissociation pressure (P_{diss}). Evidently each hydrate is characterised at a given temperature by a definite value of P_{diss}. In principle

$$P_{diss} = P'_M + P'_{H_2O},$$

where P'_M is the vapour pressure of the hydrate-forming substance M over the hydrate and P'_{H_2O} the vapour pressure of the water above the crystal lattice of the same hydrate, constructed from H_2O molecules. In practice, $P_{diss} \simeq P'_M$ (since $P'_M \gg P'_{H_2O}$).

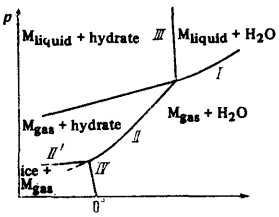

Figure 3. P–t phase diagram.

From what has been said above, at constant temperature there are two boundary conditions[48], which determine the possibility of existence of a hydrate: (1) $P'_M < P_M$, and (2) $P'_{H_2O} < P_{H_2O}$, that is, the equilibrium pressure of the vapour of M above the solid hydrate (P'_M) should be less than the pressure P_M in the system, and simultaneously the equilibrium pressure of water vapour above the hydrate crystal (P'_{H_2O}) should be less than the partial pressure of water vapour (P_{H_2O}) in the same system. Investigations made by many authors have shown[4,5] that this second condition is observed in practice only for the presence of drops of liquid water in the system (that is, at 100% humidity at the given temperature).

The relation between the equilibrium pressure of the hydrate-forming substance over the hydrate (in the literature it is usually denoted simply by the symbol P) and the temperature is described by the well-known equation[49-51]:

$$\lg P = A - B/T,$$

where T is in °K. Tamman and Kriege[52] showed that for most gas hydrates the connection between the equilibrium pressure and temperature can be represented by an equation of the type:

$$t = a(\lg P + B).$$

Diagrams[53] constructed on a semilogarithmic scale for methane, ethane, propane, and isobutane well reflect the linear character of the relation between $\lg P$ and t and allow the equilibrium conditions for hydrate formation for each of these hydrocarbons to be found readily by interpolation.

§ For hydrates of structure (I) $dt/dp > 0$; for structure (II) $dt/dp < 0$.[10]

IV. METHODS OF PREPARATION AND OF DETERMINING THE COMPOSITION OF HYDRATES

Experimental methods for the preparation of hydrates are considered in the papers of Frost and Deaton[51], Hammerschmidt[4], and the reviews of Czaplinski[2,3]. Hydrates can be formed both in a closed system (most convenient for laboratory investigations) and in a flow system (gas pipes, petrochemical industrial plant).

The formation of hydrates can in principle be compared with crystallisation from a supersaturated solution or the freezing of a supercooled melt[2]. Therefore the general rules formulated by Eucken[54] for crystallisation can be transferred to the process of hydrate formation. This process is greatly facilitated[4] by increasing the rate of gas flow, saturation with water vapour, pressure pulsations, the introduction of small crystals of the hydrate or other nuclei for the crystallisation (for example, crystallites of AgI[55]).

From the very definition of gas hydrates as non-stoichiometric clathrates it follows that in the formula $M.nH_2O$ the value of n is variable¶, depending on the degree of filling of the cavities†. The minimal value of n is reached when all the cavities of the clathrate crystal are filled with molecules of the hydrate-forming substance.

In this sense it is possible to speak about the "ideal" formula of the hydrate. For hydrates of structure (I) the ideal formula $8M.46H_2O$ or $M.5.75H_2O$ (when only the six large cavities are filled, $6M.46H_2O$ or $M.7\frac{2}{3}H_2O$). For the hydrates of structure (II) the eight large cavities ($d_{eff} < 6.7$ Å) are usually filled and the ideal formula of such a hydrate is $8M.136H_2O$ or $M.17H_2O$.

1. DIRECT EXPERIMENTAL DETERMINATION OF COMPOSITION

The direct determination of the composition of a hydrate is carried out as follows[2,51]: a definite quantity of liquid water and of compressed gas is put in a thick-walled glass tube at ~ 0°C and, with periodic shaking, the system is kept for several days. After complete bonding of the water in the hydrate the tube is cooled below the temperature at which $P_{diss} = 1$ atm, and the excess of gas, bonded with the water, is removed. Then the hydrate is decomposed by heating and the volume of gas liberated is measured, after which the composition of the hydrate is calculated from the ratio between the initial amount of water and the volume of gas liberated.

It should be noted that for any one hydrate many authors have obtained quite different results[51,55]. The explanation is firstly that the conditions of carrying out the experiment are not comparable and secondly the serious experimental difficulties that arise in carrying out the method. Of the many studies devoted to the direct experimental determination of the composition of hydrates, the most precise are those of Marshall and coworkers[57] and Ceccoti[55]. The former determined the composition of methane hydrate in the pressure range 150–680 atm, and in the calculations they took account of the compressibility of methane and its solubility in water. The same authors observed an interesting fact: the occlusion of water by the hydrate lattice which is formed prevents the interaction between gas and water proceeding to completion.

Ceccoti studied the formation of hydrates by propane directly in the gas phase in the presence of microcrystallites of AgI, which, as he showed, serve as effective catalysts for hydrate formation. In this instance the result of the experiment was not distorted by the occlusion of the liquid phase (aqueous or hydrocarbon) of the crystal lattice of the hydrate. At a temperature somewhat above the lower quadruple point the propane hydrate was found to have the composition $C_3H_8 . 19.7H_2O$ (which corresponds to 86% filling of the large cavities). Ceccoti first suggested that propane hydrate, by analogy with bromine hydrate[58], has a tetragonal structure. A method first proposed by Bigorné[59] belongs among the direct experimental methods of determining the composition of hydrates. He found that when the hydrate is formed from an aqueous solution of a salt (for example, $NiSO_4$), which does not itself react with a hydrate-forming substance (ClO_2), then after the formation of the hydrate the quantity of "free" water in the system decreases, since part of it is converted into the hydrate lattice, but the concentration of the salt in the solution rises correspondingly. Knowing the decrease in the hydrate-forming substance in the system, it is easy to calculate the composition of the hydrate. The precision work of Khayano and Takasi[60] was based on the principle stated above; they determined the composition of isobutane hydrate ($M.17.1H_2O$) with the aid of a series of NaCl solutions of different concentration.

2. SEMIEMPIRICAL METHOD OF CALCULATING THE COMPOSITION OF HYDRATES

This method, first proposed by de Forcrand[61] and perfecte by Scheffer and Meyer[62], allows the value of n at the lower quadruple point to be determined, that is, the point of intersection of the two curves "ice–hydrate–gas" and "water–hydrate–gas". As stated above, each of these curves is described by an equation of the type $\lg P = A - B/T$, in which the constants A and B are found by experiment. The number of water molecules connected with one molecule of the hydrate-forming substance is calculated by the simple formula:

$$n = \frac{\Delta H_1 - \Delta H_2}{Q},$$

where ΔH_1 and ΔH_2 are the molar heats of formation of the hydrate from liquid water and from ice, and Q is the molar heat of fusion of ice (at 0°C, $Q = 1430$ cal mole^{-1}). The values of ΔH_1 and ΔH_2 for the specific hydrate were calculated in the usual way, by combining the equation given above with the Clausing–Clapeyron equation:

$$T\frac{\Delta P}{\Delta T} = \frac{\Delta H}{\Delta V}.$$

In this way the compositions of the hydrates of methane, ethane, propane, and natural gas were determined for the lower quadruple point[49–51].

In the same way van Cleef and Diepen[31] calculated the composition of the hydrates of oxygen and nitrogen which they obtained for the first time at high pressures. The calculations were sufficiently rigorous: the density of the hydrated crystals, the solubility of the gas in water, and its coefficient of compressibility were calculated. For nitrogen hydrate at the lower quadruple point ($t = -1.3$ °C, $P = 141.5$ atm) the composition $N_2(6.01 \pm 0.23)H_2O$ was

¶ According to van der Waals (grandson) and Platteeuw[28,55], with rise in temperature along curves *II* and *III* on the *P–t* diagram the degree of filling of the cavities of the hydrate lattice increases, that is, the value of n decreases.

† When a hydrate is formed directly from an aqueous solution, for example, ethylene oxide hydrate[56].

found and for oxygen hydrate ($t = -1.0°C$, $P = 104.2$ atm), the value $n = 6.06 \pm 0.21$.

It is interesting to note that even at $P > 100$ atm not all the cavities of the hydrate lattice are completely filled.

Among the indirect methods of determining n must be included the method proposed by Miller and Strong[48].

On applying the law of mass action to the formation of propane hydrate

$$C_3H_8 + nH_2O \rightleftarrows C_3H_8 \cdot nH_2O\,(\text{hydr.})$$

in terms of activities

$$[a_{C_3H_8}][a_{H_2O}]^n = K[a_{C_3H_8} \cdot n_{H_2O}]$$

and then converting to fugacities the authors obtained the expression:

$$f_2(a)^n = f_1(a_1)^n = K,$$

where f_2 is the fugacity of propane in equilibrium with the hydrate and pure liquid water, f_1 the fugacity of propane in equilibrium with the hydrate in aqueous solution, a the activity of pure liquid water ($a = 1$), and a_1 the activity of water in the solution. From the equation given above,

$$n = \frac{\lg (f_2/f_1)}{\lg (a_1/a)} = \frac{\lg f_1 - \lg f_2}{-\lg a_1}.$$

By using aqueous 2 M solutions of methanol, ethanol, acetone, and KOH for hydrate formation, Strong and Miller obtained at 1.9°C for all four solutions the value $n \simeq 6$. It should be noted that this result does not agree with the values of n for propane hydrate found by other investigators[51] ($n = 17.95$).

V. THERMODYNAMICS OF HYDRATE FORMATION

Problems connected with the calculation of the energy of formation of hydrates, the entropy and enthalpy of this process, and the work of expansion of the crystal lattice of the hydrate were considered in detail by Stackelberg[13]. On the basis of the general premises that simple gas hydrates are formed from molecules of water and the hydrate-forming substance with the aid of van der Waals forces and that in energetic respects the crystal lattice of the gas hydrate differs very little from the lattice of ordinary ice[12]. Stackelberg suggested that the entropy of the reaction:

$$M_{gas} + nH_2O_{solid} = M.nH_2O_{hydr.}$$

equals the entropy of freezing of 1 mole of gas (ΔS):

$$\Delta S = \Delta S_1 + \Delta S_2.$$

In this instance ΔS_1 (the entropy of condensation of 1 mole of gas) according to Trouton's rule is 21 cal deg^{-1} and ΔS_2 (entropy of freezing of 1 mole of liquefied gas) was 1 cal deg^{-1}, and consequently $\Delta S = -22$ cal deg^{-1}. By analogy with physical adsorption, according to Eucken[54] the energy of formation of the hydrate is

$$W_{ads} = W_{hydr} \simeq -\sqrt{21 T_b} \times 8000,$$

where T_b is the boiling point of the hydrate-forming substance at atmospheric pressure in °K, 8000 cal mole^{-1} is the heat of vaporisation of water not entering into the pseudocrystalline group; hence $W_{hydr} \simeq -400\sqrt{T_b}$.

The change in free energy (ΔG) in hydrate formation is here described by the equation (for 273°K):

$$\Delta G = W_{hydr} - T\Delta S = -400\sqrt{T_b} + 6000. \quad (1)$$

At the same time

$$\Delta G = RT \ln P_{diss}, \quad (2)$$

where P_{diss} is the dissociation pressure of the hydrate in atmospheres.

On combining Eqns. (1) and (2) it is easy to obtain the relation

$$\lg P_{diss.} = 4.8 - 0.32\sqrt{T_b}. \quad (3)$$

Eqn. (3), which connects P_{diss} with the boiling point of the hydrate-forming substance, is true only at 0°C.

For $t > 0°C$ ($M_{gas} + nH_2O_{liquid} \rightarrow M.nH_2O_{hydr}$), Stackelberg obtained the general equation:

$$4.57 \lg P_{diss.} = -400\sqrt{T_b} - n1437 + 22T + 1437T/273. \quad (4)$$

With the aid of Eqn. (3) he calculated P_{diss} at 0°C for hydrates which had been studied well and obtained values which were compared with experimental data (Table 1).

Table 1.

M	B.p., T_b, °K	P_{diss}, atm	
		expt	calc.
CH_4	112.0	26	26
C_2H_4	171.0	5.5	4.2
C_2H_6	180.0	5.2	3.2
C_2H_2	189.0	5.7	2.5
C_3H_8	228.0	1.0 (1.7)	0.9

As noted above, one of the main conditions for the existence of a hydrate is the relation[48]: $P'_M = P_{diss} < P_M$, where P_M is the saturated vapour pressure of the hydrate-forming substance.

By using the combined Clausing–Clapeyron and Trouton equation $\lg P_M = 4.60 - 0.0169\, t_b$ and Eqn. (3) the boundary condition for the formation of the hydrate can be obtained ($P_M = P_{diss}$): $t_b = 60°C$. Hence gases and volatile organic liquids with $t_b > 60°C$ cannot form hydrates. The extensive experimental results agree with this statement (an exception is chloroform, for which $t_b = 61°C$).

ENTHALPY OF FORMATION OF HYDRATES

Stackelberg showed[7,13] that for the process $M_{gas} + nH_2O_{liquid} \rightleftharpoons M.nH_2O_{hydr}$ the enthalpy calculated on the basis of calorimetric and tensimetric measurements for $n \simeq 6$, varies within limits from −14 to −17 kcal mole^{-1}; at $n \simeq 9$, from −19 to −20 kcal mole^{-1} and at $n \simeq 17$, from −29 to −32 kcal mole^{-1}. For the process $M_{solid} + nH_2O_{solid} \rightleftharpoons M.nH_2O_{hydr}$ both the enthalpy (±2 kcal mole^{-1}) and entropy (±5 cal deg^{-1}) are almost equal to zero. Simultaneously with this Stackelberg found that for the formation of "double hydrates":

$$M_{gas} + 2H_2S_{gas} + 17H_2O_{liquid} \rightleftarrows M \cdot 2H_2S \cdot 17H_2O_{hydr},$$

the enthalpy and entropy are rather significant ($\Delta H =$ 70 kcal mole^{-1} and $\Delta S = -200 - 250$ cal deg^{-1}).

The work of expansion of the crystal lattice of the hydrate on increasing the diameter of the molecule introduced into its internal cavities was calculated by Stackelberg and Jahns[14].

As a result of careful X-ray diffraction measurements of the crystal lattice parameters of the hydrates of structures (I) and (II) they found that the parameters a increase with the diameter of the molecule of the hydrate-forming substance. Thus a change in d_{eff} from 5.2 to 5.7 Å increases the lattice parameter of structure (I) by 1%. The same effect is observed in structure (II) for "double hydrates", where the increase in a becomes noticeable at $d_{eff} > 6.3$ Å. Evidently the value of the work of expansion of the crystal lattice of the hydrate produced by large molecules allows the stability of the hydrate to be evaluated.

Starting from the general definition, the work of expansion is $-W_{exp} = \int_{v_0}^{v} p\,dv$, where p is the dissociation pressure of the hydrate, and introducing the value of the coefficient of compressibility of the hydrate, which characterises the force opposing the expansion of the lattice,

$$\chi = -\frac{1}{v_0}\cdot\frac{dv}{dp},$$

the authors[14] obtained the following expression for the work of expansion:

$$-W_{exp.} = \frac{[9Na_0^4(\Delta a)^2]}{8\cdot 2\cdot\chi\cdot a_0^3\cdot 41} = \frac{8{,}3\cdot 10^{21}\cdot a_0^3}{\chi}\left(\frac{\Delta a}{a_0}\right)^2 \text{ cal}, \quad (5)$$

where a_0 is the parameter of the normal lattice (before expansion), $a = a_0 + \Delta a$ is the parameter of the expanded lattice.

On converting to numerical values: $\chi = 4\times 10^{-5}$, $a_0 = 12\times 10^{-8}$ cm, structure (I), and $a_0 = 17.3\times 10^{-8}$ cm, structure (II), the final form can be obtained.

$$-W_{I} = 36\left(100\frac{\Delta a}{a_0}\right)^2 \text{ cal, structure (I)} \quad (6)$$

$$-W_{II} = 107\left(100\frac{\Delta a}{a_0}\right)^2 \text{ cal, structure (II).} \quad (7)$$

The work performed in the expansion of the crystal lattice increases the chemical potential of the molecule of the complex-forming substance by $\Delta\mu$:

$$-W_{exp} = \Delta\mu = RT\ln(P/P_0). \quad (8)$$

From this equation, on increasing the chemical potential, P_{diss} for the hydrate increases and consequently the "upper quadruple point" of the hydrate is shifted to lower temperatures. This depression of the critical temperature for the decomposition of the hydrate (ΔT_C) is described by the equation:

$$\Delta T = (-W_{exp}\cdot T)/(\lambda_{hydr} - \lambda_M) = -W_{exp}\cdot T/\lambda \quad (9)$$

where λ_{hydr} is the heat of the reaction $M.nH_2O \rightarrow M_{gas} + nH_2O_{liquid}$; λ_M the heat of vaporisation of the hydrate-forming substance, and λ the heat of the reaction $M.nH_2O \rightarrow M_{liquid} + nH_2O$.

For structure (I) (at $n \simeq 6$), $\lambda_I \simeq 10\,000$ cal, λ_{II} (at $n \simeq 17$) = 25 000 cal, and consequently after substituting in Eqn. (9) the corresponding values of W^{I}_{exp} and W^{II}_{exp} the approximate formula

$$\Delta T = 1.1\left(100\frac{\Delta a}{a_0}\right)^2 \quad (10)$$

can be obtained; it is true for structures (I) and (II).

From Eqn. (10) it follows that an increase of 3% in the lattice dimensions depresses the temperature of the upper quadruple point by 10 deg. This conclusion agrees with the experimental results[14].

VI. STABILISATION OF HYDRATES WITH THE AID OF AN "AUXILIARY GAS"

The stabilising action on hydrate formation of a so-called "auxiliary gas", that is, a gas the molecules of which are not held in the internal cavities of the hydrate crystal, was first observed by Villard in 1897.[63] In studying the hydrate of N_2O, Villard found that in pure compressed N_2O at 14°C the decomposition pressure of the hydrate formed is 250 atm.

When the experiment is carried out at the same temperature but in the presence of air the decomposition pressure of the hydrate is reduced to 100 atm. In 1923 Villard[1] observed a still more interesting effect: iodine, which itself is incapable of hydrate formation (b.p. 183°C), forms in the presence of oxygen or nitrogen (which form hydrates only at very high pressures[31]) a brick-red, crystalline hydrate, stable at 3°C (P_{N_2} = 200 atm) and even at 8°C (P_{O_2} = 330 atm). Further investigations of the "stabilisation effect" carried out by Stackelberg and Meinhold[11] allowed a general experimental rule to be established: certain gases (N_2, O_2, CO_2, etc.) which fill only an insignificant part of the cavities of the hydrate lattice appreciably raise the critical temperature for the decomposition of a hydrate by their presence (usually at $P > 1$ atm). The degree of elevation of the decomposition temperature of the hydrate depends on the nature of the gas. Thus in studying the influence of CO_2 and N_2 on the decomposition temperature of hydrates (CCl_4, $CHCl_3$, CH_2Cl_2)‡ Stackelberg and Meinhold established that the effect which could be produced by the presence of CO_2 is twice as much as that obtainable in the presence of N_2 (~ 10 deg and 5 deg). It is also interesting to note that the stabilising influence of n-butane§, which was recently unambiguously shown not to form hydrates itself[60], but nevertheless on being present as one of the components of a gaseous mixture considerably alters the value of the equilibrium pressure over the "mixed hydrate". Extensive investigations of the stabilising action of "auxiliary gases" were made by Barrer and Ružicka[64]. In studying the hydrates of chloroform the authors established that such gases as H_2, Ne, N_2, Ar, O_2, CH_4, Kr, Xe, C_2H_4, C_2H_6, and CO_2 not only appreciably change the equilibrium conditions of hydrate formation but also partially fill the small cavities of structure (II), that is, here it is possible to speak not about an individual hydrate of chloroform but about its "mixed hydrates".

VII. HYDRATES OF INDIVIDUAL GASES AND VOLATILE ORGANIC LIQUIDS

Schroeder's monograph[1] contains the most complete information about the hydrates of the individual gases and the volatile organic liquids relating to the experimental results published up to 1923. Frost and Deaton's monograph[5] contains data embracing the period up to 1945 and relating mainly to hydrates of hydrocarbon gases. The studies made in the last two decades are surveyed in the review part of Stackelberg's papers[10,11], the fundamental handbook edited by Katz[65], and also in a series of articles published between 1960 and 1966.

‡ Carbon tetrachloride forms hydrates only in the presence of a stabilising gas.

§ In this connection indications of the possibility of the formation of hydrates of n-butane[3,53] must be considered extremely doubtful.

Methane

Villard first obtained a hydrate of methane[66] at $t > 0°C$ and $P > 1$ atm; the maximal temperature at which he succeeded in obtaining the hydrate was 21.5°C. Methane hydrate was then investigated by Deaton and Frost[67] and Roberts[68] who studied the $P-t$ dependence for temperatures from 0.5° to 12.8°C. The part of the $P-t$ diagram in the region of existence of ice (from −10° to −5°C) was also investigated[68]. The construction of apparatus needed for working at high pressures allowed Kobayashi and Katz[69,70] to obtain the $P-t$ dependence at pressures from 333 atm (22.5°C) to 762 (28.8°C).

Campbell and McLeod[71] studied methane hydrate in the same pressure interval and obtained results agreeing with those of Kobayashi and Katz. In 1964, Marshall and coworkers published a study[72] in which with the aid of a specially constructed chamber, using an original method of "pressure jump" they studied hydrates of CH_4 in the pressure range from 157 atm (17°C) to 3915 atm (47°C). Table 2 gives their equilibrium $P-t$ data.

Table 2.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
17.05	157	28.44	645.3
17.33	157.2	33.55	1093.1
22.05	295.8	37.16	1506.2
21.94	295.1	39.55	1847.2
22.61	332.8	40.5	2033.0
24.9	437.0	41.05	2208.3
25.0	431.8	43.66	2679.2
27.0	561.3	45.16	3152.8
28.4	645.3	46.44	3627.1
		46.88	3915.4

In their monograph[28] van der Waals and Platteeuw give the following physicochemical characteristics for the hydrate of CH_4, structure (I): $P_{diss} = 26$ atm at 0°C; the heat of formation from water and the gas is 14.5 kcal mole^{-1} at 0°C; the decomposition temperature at $P = 1$ atm is $t = -29.0°C$.

Ethane

The hydrate of C_2H_6 was first obtained by Villard[73]. Deaton and Frost[74] obtained the $P-t$ dependence for ethane hydrate at pressures of 5.4–54 atm and temperatures 0–14.4°C. Roberts[68] studied ethane hydrate at pressures up to 64 atm (this also embraces the region of existence of the liquid hydrocarbon phase). Deaton and Frost[51] obtained equilibrium $P-t$ data in the region of negative temperatures; they investigated temperatures from −9.6° to −1.1°C and pressures from 3.09 to 4.51 atm. Their results are presented in Table 3.

On the basis of the equilibrium data given above and obtained earlier[74,75] for $t > 0°C$ and pressures up to $P =$ 68 atm, Deaton and Frost calculated the heats of decomposition of ethane hydrate at $t > 0°C$ (17 796 cal mole^{-1}) and $t < 0°C$ (6069 cal mole^{-1}) and used Forcrand's method to determine the composition of the hydrate at the lower quadruple point: $C_2H_6 \cdot 8.25H_2O$. The most recent results on the equilibrium $P-t$ data are given in Reamer and coworkers' work, carried out at a high experimental level. These results, which agree well with those obtained by other authors, are given in Table 4.

The following constants for ethane hydrate, structure (I), are given by van der Waals and Platteeuw[28]: $P_{diss} = 5.2$ atm at 0°C; maximal temperature of existence of the hydrate 14.5°C; heat of hydrate formation at 0°C, $\Delta H = 16.3$ kcal mole^{-1}.

Table 3.

t_{equil}, °C	P_{equil}, atm
−9.6	3.09
−6 6	3.52
−3.5	3.99
−1.1	4.51

Table 4.

t_{equil}, °C	P_{equil}, atm
6.73	9.6
9.66	16.42
11.52	21
14.2	32.5

Table 5.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
1.5	9.26	9.6	23.75
5.22	11.41	9.76	24.7
5.16	12.18	10.2	29.1
5.55	13.81	10.5*	26.2*
6.11	17 5	11.5	30.9
6.5	20.5	12.05	32.2
7.26*	19.1*	19.93	34.9
8.55	21.9		

* Values of P_{equil} too low.

Stackelberg gave[10] $\Delta H = 15.0$ kcal mole^{-1}, decomposition temperature of hydrate $t = 15.8°C$ at $P = 1$ atm.

Ethylene

Ethylene hydrate was first obtained by Villard[66], who determined P_{diss} for the hydrate at 0° and 17°C (5.5 atm and 44.8 atm). More extensive investigations in this field were made by Deaton and Frost[67], Kobayashi and Katz[69], and by Diepen and Scheffer[77], who investigated ethylene hydrate at pressures up to 50.5 atm. Reamer and coworkers[76] made a careful determination of the equilibrium $P-t$ values; their results are given in Table 5.

Snell and coworkers[78] studied the conditions of formation of ethylene hydrate and of the hydrate of a $CH_4 + C_2H_4$ mixture at pressures up to 612 atm. Fig. 4 shows the $P-t$ dependence they obtained.

Stackelberg[10] gives the following values of the constants for ethylene hydrate, structure (I); $P_{diss} = 5.5$ atm at 0°C (5.44 according to Diepen), $\Delta H = 15.2$ kcal mole^{-1}; decomposition temperature −13.4°C at $P = 1$ atm; composition found by Claussen[20] by an X-ray diffraction method $C_2H_4 \cdot 7.4H_2O$.

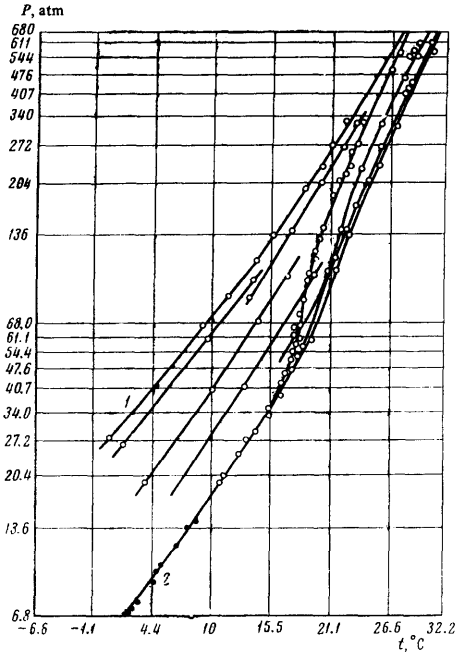

Figure 4. Conditions of formation of the mixed hydrate of CH_4 (*1*) and C_2H_4 (*2*).

Acetylene

Acetylene hydrate was first obtained from the compressed gas in 1877 by Cailletet[1]. Villard[73] measured the pressure of C_2H_2 vapour over its hydrate at 0°C (P = 5.5 atm) and 17°C (P = 44.8 atm). In a summary table Stackelberg[10] gives: (a) decomposition temperature of hydrate 15.4°C at P = 1 atm; (b) temperature of upper quadruple point, 16°C; (c) heat of formation of hydrate 15 000 cal mole^{-1}.

Propane

Propane hydrate was first obtained by Villard[73]. Deaton and Frost determined the equilibrium P–t values for this hydrate[74,75] (Table 6). On the basis of the P–t values given above the heats of formation of propane hydrate at $t > 0$°C and $t < 0$°C and its composition at the lower quadruple point ($C_3H_8 \cdot 17.95H_2O$) were calculated[79].

The conditions of formation of propane hydrate at high pressures (in the region of existence of the liquid hydrocarbon phase) were also studied by Wilcox and coworkers[79], Reamer and coworkers[76] (at temperatures from 1.1° to 5.7°C and pressures from 2.4 to 20 atm), and Teodorovich[80].

The following values of the constants for propane hydrate structure (II), are given by van der Waals and Platteeuw[28]: P_{diss} = 1.74 atm at 0°C (Stackelberg[10] gave P_{diss} = 1 atm), maximal temperature of existence of hydrate t = 5.69°C, heat of formation 32 000 cal mole^{-1} at 0°C, crystal lattice constant 17.4 Å.

Propene

The first information about propene hydrate is contained in a paper by Reamer and coworkers[76]. They succeeded in obtaining P–t values for the pressure range 5–20 atm and temperatures from 0.5° to 1.7°C (the pressure interval also embraces the region of existence of the liquid hydrocarbon phase). A precision investigation of propene hydrate, during which even the pressure of water vapour in the system was calculated, was made by Clarke and coworkers[81]. Table 7 gives their equilibrium results. They obtained the following expression for the volatility (f) of propene over its hydrate:

$$\lg f = 24.8309 \pm 0.0001 - (6610 \pm 20)\ 1/T$$

Table 6.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−11.95	0.984	+0.222	1.787
− 9.0	1.137	+0.444	1.895
− 6.27	1.318	+0.611	1.901
− 5.56	1.328	+0.723	2.018
− 3.33	1.462	+2.388	2.875
− 0.278	1.698	+3.78	3.958

Table 7.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−0.161	4.569	0.493	5.330
−0.134	—	0.558	5.404
−0.113	4.622	0.594	5.452
−0.064	4.674	0.798	5.709
+0.006	4.746	0.897	5.851
0.217	4.988	0.943	5.913
0.325	5.114	0.958	—
0.442	5.253		

and calculated the heat of decomposition of the hydrate at t = 0°C (ΔH = 30230 ± 90 cal mole^{-1}). P–t values in the range of negative temperatures (from −3.7° to −14.7°C) were found by Byk and coworkers[82], who obtained an equation for the above temperature range, $\lg f = 4.4853 - 1072/T$ and calculated the heat of decomposition of the hydrate for $t < 0$°C (ΔH = 4920 cal mole^{-1}).

According to Clarke and coworkers[81] the temperature of the lower quadruple point of propene hydrate is −0.134°C, that of the upper is 0.958°C, and the composition of the hydrate is $C_3H_8 \cdot 17H_2O$.

Isobutane

Deaton and Frost obtained the first reliable experimental equilibrium P–t data for isobutane hydrate[83]. Kayano and Utida[60] made a careful investigation of isobutane hydrate, including the determination of its composition (iso-$C_4H_{10} \cdot 17H_2O$ and quadruple points (0°C and 847 mmHg for the lower point; 1.8°C and 1268 mmHg for the upper); they obtained the following equations:

$$\lg P_{mm} = 29.33 - 7210/T \ (\text{at } t > 0°),$$
$$\lg P_{mm} = 9.106 - 1688/T \ (\text{at } t < 0°).$$

Their calculated heats of decomposition of the hydrate are respectively ΔH = 32 960 cal mole^{-1} (t > °C) and ΔH = 7716 cal mole^{-1} (t < 0°C).

Hydrogen Sulphide

Hydrogen sulphide hydrate was first obtained in 1840 by Beller[1]. Systematic investigations of this hydrate were carried out by de Forcrand and Villard[84], who measured P_{diss} of the hydrate at 0.5°C (1.1 atm) and 28.5°C (16 atm). Sheffer[85] determined the quadruple points of the hydrate (−0.389°C and 0.917 atm for the lower point; 29.6°C and 22 atm for the upper), and Kolvezce and Scheffer[86] its composition: $H_2S.6H_2O$.

Careful measurements of the equilibrium P–t values (the water–hydrate–H_2S_{gas} system in the region close to the freezing point of water) were made by Wright and Maas[87].

The most extensive investigation of the H_2S–H_2O system (in the region of existence of the hydrates) was made by Selleck and coworkers[88], who obtained equilibrium P–t values for the temperature range from −0.389° to 29.45°C and pressures from 0.917 to 22.10 atm. These results are given in Table 8.

Table 8.

Hydrate–water–gas		Hydrate–ice–gas	
t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
− 0.389*	0.917	0	0.435
+ 4.4	1.55	−15	0.496
+10	2.75	−12.2	0.556
+15.5	5.925	− 9.45	0.631
+21.1	8.79	− 6.6	0.714
+26.6	15.7	− 3.89	0.803
+29.6*	22.0	− 1.11	0.891
− 0.389	0.917*	− 0.233*	0.917
+ 1.8	3.4	−22.7	0.340
+18.6	6.8	—	—
+22.6	10.2		
+25.3	13.6		
+27.4	17		
+28.8	20.4		
+29.45	22.10*		

* Quadruple point.

For the system hydrate + H_2O_{liquid} + H_2S_{gas} these same authors obtained the equation:

$$\lg P_{atm} = 15.11835 - \frac{6867.98}{T}.$$

Sulphur Dioxide

Sulphur dioxide hydrate, with m.p. 4–5°C was obtained in 1829.[1] Having obtained a hydrate from liquid SO_2, Villard[73] proposed the formula $SO_2.6H_2O$. Roozeboom[47] determined, in a sealed glass ampoule, the critical decomposition temperature of SO_2 hydrate (12.1°C) and the decomposition temperature at P_{SO_2} = 1 atm (7.1°C).

Tamman and Kriege[52] proposed for sulphur dioxide hydrate the equations $t = 16.75\,(\lg P + 0.4179)$ at $t > -2.6$°C, and $t = 41.60\,(\lg P + 0.4904)$ at $t < -2.6$°C, where t is the temperature of hydrate formation, and P the dissociation pressure, atm. The same authors found that $t = -2.6$°C is the eutectic point, at which the hydrate has the composition $SO_2.6H_2O$. Stackelberg[10] gives the following values for the constants of sulphur dioxide hydrate, structure (I): P_{diss} = 0.39 atm at 0°C; heat of hydrate formation from gaseous SO_2 and H_2O = 16.6 kcal mole^{-1}, crystal lattice constant 11.94 Å.

Carbon Dioxide

Carbon dioxide hydrate was obtained in 1882 by Wroblewsky[89] at ~ 0°C and a CO_2 pressure of ~ 30 atm. Villard[76] proposed the formula $CO_2.6H_2O$ for the hydrate Tamman and Kriege[52] measured P_{diss} of the hydrate in the temperature range from −20° to −43°C (106.4 mmHg and 9.2 mmHg) and obtained the equation $t = 22.0\,(\lg P - 1.0904)$, where t is in °C and P in cmHg.

Wiebe[90], having studied the CO_2 + H_2O system at pressures up to 700 atm, obtained for carbon dioxide hydrate the formula $CO_2.7H_2O$. Deaton and Frost[74] obtained equilibrium P–t data for a wide temperature range (including $t > 0$°C).

Table 9.

t_{equil}, °C	P_{equil}, atm
4.6	20.1
6.0	25.5
7.7	31.8
9.2	36.4
9.2	42.4

Unruch and Katz[91] studied the conditions of hydrate formation in the CO_2 + H_2O system up to the upper quadruple point (9.8°C, 42.4 atm). Their results are given in Table 9.

Dinitrogen Oxide (N_2O)

Villard obtained dinitrogen oxide hydrate in 1888.[79] He measured P_{diss} of this hydrate at −9.1°C (P_{diss} = 3.6 atm) and 10.7°C (P_{diss} = 34.7 atm), and also proposed for it the formula $N_2O.6H_2O$. Tamman and Kriege[52] obtained for dinitrogen oxide hydrate the equation:

$$t = 1.9\,(\lg P - 0.9795),$$

where t is in °C, and P_{diss} in atm.

Stackelberg[10] gives the following constants for dinitrogen oxide hydrate, structure (I): P_{diss} = 10 atm at 0°C, decomposition temperature −19.3°C at P_{N_2O} = 1 atm. The critical decomposition temperature is 12.0°C, the heat of formation of the hydrate (from water and gas) 14.7 kcal mole^{-1}. The crystal lattice constant is 12.03 Å.

Hydrogen Selenide (H_2Se)

Hydrogen selenide hydrate was obtained by de Forcrand in 1902.[1] Experimental P–t values have not been published. Stackelberg[10] gives the following constants for this hydrate: P_{diss} = 0.45 atm at 0°C, decomposition temperature of the hydrate 8.0°C at P = 1 atm; t_c = 30°C; lattice parameter 12.06 Å.

Sulphur Hexafluoride (SF_6)

Sulphur hexafluoride hydrate was studied by Sortland and Robinson[36]. The authors obtained $P-t$ data for the temperature range from −9 to 15° they calculated the composition of the hydrate at the lower (~ 0°C) quadruple point: $SF_6.17.02H_2O$, determined the upper quadruple point (14.0°C, 19.9 atm), and also calculated the heat of formation of the hydrate at $t < 0$°C (5140 cal mole^{-1}) and at $t > 0$°C (29570 cal mole^{-1}).

PH_3, AsH_3, and SbH_3

1. Phosphine hydrate was obtained by Skinner[1] by condensing phosphine vapour in the presence of water. The same author measured P_{diss} at 1°C (P = 2 atm) and 25.0°C (P = 16 atm).

According to Stackelberg[10] P_{diss} = 1.6 atm at 0°C, decomposition temperature of the hydrate = −6.4°C at P_{PH_3} = 1 atm, critical decomposition temperature = 28.0°C.

2. According to Schroeder[1] arsine hydrate has the composition $AsH_3 . 6.14H_2O$ and is characterised by the following values: t = 0°C at P = 613 mmHg; t = 1.6°C at P = 760 mmHg; t = 21°C at P = 8.85 atm.

According to Stackelberg[10], the constants of arsine hydrate are: decomposition temperature = −1.8°C at P = 1 atm. Critical decomposition temperature 28.3°C.

3. For stibine hydrate, Schroeder[1] gives the value P_{diss} = 760 mmHg at t = 10.9°C.

Chlorine

Chlorine hydrate, as already stated above[1], was obtained in 1810 by Davy. The decomposition temperature of this hydrate (determined in a sealed glass ampoule) is 28.7°C, according to Schroeder[92].

van der Waals and Platteeuw[28] give data for chlorine hydrate: P_{diss} = 252 mmHg at 0°C; heat of formation 16.0 kcal mole^{-1}; crystal lattice parameter 12.03 Å. Tamman and Kriege[52] proposed for this hydrate the formula $Cl_2.8H_2O$ and for $t < 0$°C (the ice–hydrate–vapour system) obtained the equation $t = 49.0\ (\lg P + 0.4757)$, where t is in °C and P in mmHg. Careful X-ray diffraction investigation of chlorine hydrate was made by Pauling and Marsh[21,93], and also Allen[94]. The latter found that at the lower quadruple point the Cl_2 molecule (for the formation of a hydrate from liquid chlorine) occupies only 16% of the small cavities of the crystal lattice, the parameter of which is 11.82 Å. The composition of this hydrate is $Cl_2 . 7.27 + 0.17H_2O$. Investigations, made by Glew and Rath[56], showed that when the hydrate is in equilibrium with gaseous chlorine, then 81% of the small cavities of structure (I) are occupied and the hydrate has the composition $Cl_2 . 6.04 \pm 0.13H_2O$.

Bromine (Br_2)

As already mentioned above, bromine hydrate was first obtained by Levig[1]. Roozeboom[47] determined the critical decomposition temperature of the hydrate (in a sealed ampoule), ~ 6.2°C, and proposed for the hydrate the formula $Br_2.10H_2O$. Tamman and Kriege[52] obtained for Br_2. $.10H_2O$ the formula $t = 43.0\ (\lg P + 0.2465)$ ($t < 0$°C), where t is in °C and P in mmHg. Mulders[28] determined P_{diss} = 43.90 mmHg at 0°C, maximal temperature of existence of the hydrate 5.81°C, heat of hydrate formation 20.83 cal mole^{-1} at 0°C and he proposed the composition $Br_2 . 8.47H_2O$ for the lower quadruple point. From Stackelberg's review[10], bromine hydrate is characterised by structure (I) with lattice parameter 12.0 Å. In addition Jeffrey and McMullan[58] proposed in 1963 that bromine hydrate crystals are tetragonal.

Iodine (I_2)

Iodine hydrate can be obtained, as was shown experimentally in 1923 by Villard[1], only in the presence of "stabilising" gases (N_2, O_2, CO_2). The highest positive temperature (8.0°C) at which the crystalline iodine hydrate is still stable could be attained in the presence of oxygen under a pressure of 300 atm.

Inert gases (Ar, Kr, Xe)

Villard obtained hydrates of Ar, Kr, and Xe in 1896[95] and then de Forcrand[96] in 1925. Nikitin[43] in 1956 also mentioned the ability of radon (Rn) to form a hydrate.

Waller[97] carried out an X-ray diffraction investigation of the hydrates of Ar, Kr, and Xe and found that all three hydrates have structure (I), with ideal formula $M . 5.75H_2O$.

Godhot[98] obtained hydrates of Kr and Xe with heavy water, $Kr.6D_2O$ and $Xe.6D_2O$.

Argon. According to Diepen, cited by van der Waals and Platteeuw[28], P_{diss} = 95.5 atm at 0°C (according to Stackelberg[10] P_{diss} = 105 atm, and the decomposition temperature of the hydrate is −42.8°C at P = 1 atm). Tamman and Kriege[52] obtained an equation for argon hydrate ($Ar.5–6H_2O$): $t = 19.6(\lg P - 2)$, where t is in °C and P in atm. The equilibrium $P-t$ values were obtained by Marshall and coworkers[72] for the wide temperature range 1.65° to 31.0°C and pressures from 105 to 3780 atm (Table 10).

Table 10.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
1.16	105.0	25.6	1807.4
3.7	130.2	26.7	2040.6
2.9	121.2	26.8	2049.8
6.3	167.6	27.7	2204.1
11.8	316.5	28.9	2662.2
11.1	314.8	29.7	3031.4
15.3	494.0	30.4	3336.7
17.8	659.9	31.0	3717.2
19.3	807.5	31.1	3777.4
23.5	1400.1	30.9	3729.1

Krypton. According to de Forcrand[96], P_{diss} = 14.5 atm at 0°C and at t = 12.5°C P_{diss} = 47.5 atm. Tamman and Kriege[52] obtained for krypton hydrate the equation: $t = 21.2\ (\lg P - 1.1698)$ where t is in °C and P in atm. Stackelberg[10] gives the following values of the constants for ($Kr.5–6H_2O$): decomposition temperature −27.8°C at P = 1 atm, heat of hydrate formation 13.9 kcal mole^{-1}.

Xenon. According to Waller's results[97] xenon hydrate is the most stable in the series Ar < Kr < Xe. de Forcrand[96] measured its P_{diss} at the temperatures 1.4°C (P = 1.45 atm) and 23.5°C (P = 17 atm). For Xe($n \simeq 6H_2O$) Stackelberg[10] gives the following values of the constants: P_{diss} 1.5 atm at 0°C (van der Waals and Platteeuw[28] give P_{diss} = 1.15 atm). The decomposition temperature of the hydrate is −3.4°C at P = 1 atm. The heat of hydrate formation is 16.7 kcal mole^{-1}; the crystal lattice parameter is 11.97 Å.

Nitrogen

As already stated above, nitrogen hydrate was first obtained by van Cleef and Diepen[30] in a specially constructed apparatus which allows hydrates to be studied at very high pressures, ~ 1000 atm. On the basis of the experimental P–t data they found for the temperature range from 0° to 18°C, they obtained the equation given below for the hydrate–water–gas system and calculated the heat of formation of the hydrate:

$$\lg P_{atm} = 14.1293 \pm 0.0006 - \frac{3257 \pm 23}{T};$$

$$\Delta H_1 = 12380 \pm 310 \text{ cal mole}^{-1}.$$

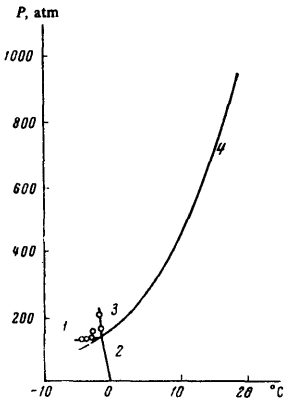

Figure 5. Conditions of hydrate formation by nitrogen: *1*) hydrate–ice–gas; *2*) ice–water–gas; *3*) hydrate–ice–water; *4*) hydrate–water–gas.

Subsequently the same authors[31] determined the equilibrium P–t values at t < 0°C for the temperature range −1.17° to −4.45°C and obtained the equation $\lg P_{atm}$ = 5.5598 ± 0.0002 − (927 ± 17)/T, calculated the heat of hydrate formation ΔH_2 = 3810 ± 110 cal mole^{-1} and also determined the lower quadruple point of the hydrate in the ice–hydrate–gas system, t = −1.3°C, P = 141.5 atm. Fig. 5 shows a correlation of the P–t results of van Cleef and Diepen for N_2.6.01 ± 0.23H_2O¶.

Nitrogen hydrates were also studied by Marshall and coworkers[57] over a wide range of temperatures and pressures. Table 11 shows their experimental P–t values.

¶ Composition of the hydrate calculated by the same authors.

Oxygen

Oxygen hydrates were first obtained by van Cleef and Diepen[31] and published P–t equilibrium data for oxygen hydrate over a wide range of temperatures from −1.8° to +18.0°C and pressures from 100 to 938 atm. The same authors proposed the equations:

$$\lg P_{atm} = 14.3082 \pm 0.0005 - \frac{3340 \pm 21}{T}$$

(for the hydrate–water–gas system), and

$$\lg P_{atm} = 5.1168 + 0.0006 - \frac{838 \pm 38}{T}$$

Table 11.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
4.4	245.2	24.6	1665
8.0	362.8	25.7	1825
13.6	628.0	26.0	2030
18.4	1005	27.4	2170
19.8	1135	29.4	2640
21.1	1270	31.6	3130
23.4	1520	32.9	3250

Table 12.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
−1.8	100.5	1.5	139	10.1	373
−1.4	104.0	1.7	142	10.1	376
−1.2	106.2	2.0	147.5	10.3	381
−1.0	108.5	2.7	158	10.6	404
−1.0	108.7	3.6	175	11.0	438
−0.8	110.6	4.7	194	12.1	471
−0.6	113.5	5.0	208	13.1	520
−0.3	116.5	5.3	214	13.2	543
0.0	119.5	5.4	214	14.1	597
0.0	120.2	6.0	232	14.2	599
0.0	120.5	7.0	260	16.0	662
0.5	126.3	8.1	296	16.1	744
0.5	127.5	8.6	308	17.1	836
1.0	136.5	8.8	320	17.6	880
				18.0	938

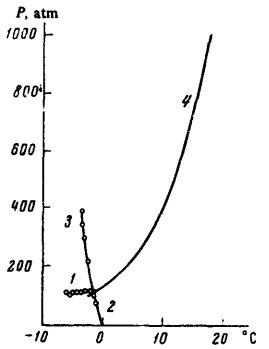

Figure 6. Conditions of hydrate formation by oxygen: *1*) hydrate–ice–gas; *2*) ice–water–gas; *3*) hydrate–ice–water; *4*) hydrate–water–gas.

(for the hydrate–ice–gas system), and calculated the heats of formation of the hydrate (O_2 . 6.06 ± 0.21H_2O): ΔH_1 = 11 840 ± 260 cal mole^{-1} and ΔH_2 = 3190 ± 160 cal mole^{-1} corresponding to the parts of the P–t curves above and

below the quadruple point ($t = -1.0°C$, $P = 109.2$ atm). The experimental results of van Cleef and Diepen are given in Table 12 and Fig. 6.

HYDRATES OF VOLATILE ORGANIC LIQUIDS

The review part of Stackelberg's paper[10] and the monograph of van der Waals and Platteeuw[28] give the characteristics of a series of hydrates formed by volatile organic liquids. All these results are given in Table 13, which also contains information about certain hydrates taken from later original papers.

Table 13.

Hydrate-forming substance	Dissociation pressure at 0°C, mmHg	Decomposition temp. of hydrate, °C, at $P = 1$ atm	Max. temp. of existence of hydrate, °C	Heat of hydrate formation at 0°C from gas and water, kcal mole^{-1}	Crystal lattice parameter, Å	Reference
CH_3Cl	311	7.5	21	18.1	12.00	
C_2H_5F	251	3.7	22.8	18.0	—	
CH_3Br	187	11.1	14.5	19.5	12.09	
CH_3SH	239	10 (8)	12	16.6	12.12	
ClO_2	160	15.0	18.2	6.5	—	
SO_2Cl_2	—	—	—	—	—	1
BrCl	125	14	—	—	—	
$CHCl_2F$	115	—	8.61	32.7	—	104*
C_2H_5Cl	201	0.78	4.8	31.9	17.30	
CH_2Cl_2	116	1.7	1.7	29	17.33	
$C_2H_4Cl_2$	555	1.5	0.09	29.4	--	
C_2H_5Br	152	1.4	0.22	—	—	
CH_3I	74	—	14.3	31.4	17.14	
$CHCl_3$	50	—	1.6	31	17.33	
$(CH_3)_2O$	—	—	—	—	17.44	
$(CH_3)_3CH$	—	—	—	—	17.53	

* $CHCl_2F.17 \pm 0.5\ H_2O$.

There are also reports[1] of the existence of hydrates of such compounds as CF_4, CHF_3, $C_2H_2F_2$, and C_2F_4. Ethylene oxide (C_2H_4O) hydrate was investigated by Glew and Rath[56] and also by Jeffrey and McMullan[58]; Glew and Rath found that the hydrate of C_2H_4O belongs to structure (I). Depending on the C_2H_4O concentration in the aqueous solution, which is found in equilibrium with the hydrate, there is a different degree of filling the cavities of the hydrate lattice. At the temperature of congruent fusion of the hydrate (11.1°C) the filling is 100% of all six of the large cavities of the crystal and 34% of the small cavities. This corresponds to the composition $C_2H_4O \cdot 6.89 \pm 0.06H_2O$.

Glew[99] studied the hydrate of bromochlorodifluoromethane ($CBrClF_2$) and found that this hydrate belongs to structure (II). Tetrahydrofuran hydrate $[CH_2]_4O.17H_2O$, was obtained by Stackelberg[18], who found its melting point to be 5.1°C.

Pinder's investigation of this hydrate[100] showed that the melting point of $[CH_2]_4O.17H_2O$ depends on the THF concentration in the equilibrium solution.

Ponyet and Mealier[101] obtained the hydrate of propylamine and Jordan and Mac[102] studied the structure of diethylamine hydrate.

McMullan and coworkers[103] investigated the hydrate of t-butylamine.

VIII. MIXED HYDRATES

As already stated above, when the hydrate-forming substance is not an individual gas, but a mixture of gases or volatile organic liquids, then the hydrate which is formed is a solution, the composition of which varies during its fusion. Such a hydrate is usually called "mixed".

The simplest examples of a "mixed hydrate" are the so-called "double hydrates" formed by a mixture of two types of molecule: $M_1 + M_2$ or $M_3 + M_4$†.

1. DOUBLE HYDRATES, FORMED BY H_2S AND H_2Se

de Forcrand[1] first observed the ability of hydrogen sulphide to form "double hydrates" when mixed with other gases. Somewhat later[1], double hydrates of hydrogen selenide were obtained. de Forcrand established the experimental fact that H_2S forms hydrates with halogen derivatives of aliphatic hydrocarbons. These hydrates are readily obtained on passing moist H_2S through the corresponding liquid at $t \simeq 0°C$.

Below, in Table 14, are listed the organic compounds which, according to de Forcrand, readily form double hydrates

Table 14.

1. CH_3Cl	8. $C(NO_2)Cl_3$	15. C_2H_5I	22. C_3H_5Br
2. CH_2Cl_2	9. C_2H_5Cl	16. C_3H_3I	23. iso-C_4H_9Cl
3. $CHCl_3$	10. $C_2H_4Cl_2$	17. C_3HCl_3	24. iso-C_4H_9Br
4. CCl_4	11. $C_2H_3Cl_3$	18. C_3H_7Cl	
5. CH_3Br	12. $C_2H_2Cl_2$	19. C_3H_7Br	
6. CH_2Br_2	13. C_2H_5Br	20. iso-C_3H_7Br	
	14. $C_2H_4Br_2$	21. C_3H_5Cl	

de Forcrand studied the $H_2S + CHCl_3$ system most carefully, having shown that the hydrates formed by this system belong to structure (II).

Lui[1] studied a group of double hydrates formed by H_2Se and halogen derivatives of hydrocarbons and found that hydrates of the type $M.2H_2Se.17H_2O$ are formed from the following compounds: CCl_4, $CHCl_3$, CH_3Br, CH_3I, C_2H_5Cl, C_2H_5Br, C_2H_5I, $C_2H_2Cl_2$, iso-C_3H_7Br, iso-C_4H_9Cl. As already stated, CCl_4 itself does not form hydrates.

At the end of the 1890s it was shown[1] that acetylene forms double hydrates with CCl_4, $CHCl_3$, $C_2H_4Cl_2$, CH_3I, $CHBr_3$, C_2H_5Br, CH_2Cl_2, and CH_2I_2.

Halogen substituted hydrocarbons also give double hydrates with C_2H_4, CO_2, and SO_2. Hydrates of such mixtures as $PH_3 + CS_2$, $PH_3 + CO_2$, and $(C_2H_5)_2O + CO_2$ are known[1]. The mixed hydrate[105] $Cl_2.Br_2.7\frac{2}{3}H_2O$, decomposition temperature 14°C, is interesting.

The double hydrates formed by H_2S with the hydrocarbons CH_4 and C_3H_8 were studied comparatively recently (1940s to 1950s). The hydrate of the mixture $CH_3 + H_2S$ was obtained by Noaker and Katz[106] and simultaneously with their obtaining equilibrium P–t values (15–19°C, 47–60 atm), the authors determined the composition of the coexisting equilibrium phases for the hydrate $2H_2S.6CH_4.46H_2O$.

The results of a study of the hydrate $2H_2S.C_3H_8.17H_2O$, which was made by van der Waals and Platteeuw in 1959[29] are of independent interest for the following reason. Up to 1959 the literature devoted to "double hydrates" had been dominated by Stackelberg's viewpoint[12], according to which

† See Chapter I of the present review.

the "double hydrates" formed by hydrogen sulphide (or H_2Se) differ from other binary mixed hydrates by their being compounds of constant composition with a definite, stable dissociation pressure at a given temperature whereas all other double hydrates are characterised by variable composition and corresponding different values of P_{dis}. Van der Waals and Platteeuw showed that the hydrate $2H_2S.C_3H_8.17H_2O$ does not differ in principle from other binary hydrates in which H_2S or H_2Se is absent and is an ordinary non-stoichiometric binary clathrate.

3. DOUBLE HYDRATES FORMED BY HYDROCARBONS

Hydrates Formed by Mixtures of Alkanes

Campbell and McLeod studied[71] hydrate formation in the binary systems: (a) $CH_4 + C_2H_6$; (b) $CH_4 + C_3H_8$; (c) CH_4 + iso-C_4H_{10}, and Deaton and Frost[5] that in the system (d) $CH_4 + C_3H_8$ and (e) $CH_4 + C_2H_6$.

System (a) was investigated at temperatures from 11.6° to 31.0°C and pressures from 68 to 680 atm (at ethane concentrations from 5.4 to 19.1%).

Table 15.

P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm	t_{equil}, °C
gas No.2		gas No.3		gas No.4	
675	28.8	676	30.9	70.4	17.4
612.5	28.02	611	29.9	61.6	19.4
475	25.8	480	281	680	30.7
339	23.4	351	25.8	340	26
239	20.4	137	20.1	476	28.3
137	16.5	103	18.5	612.5	30.5
103	14.6	69	15.6	137	21.4
71.4	11.7			103	20.1
				71.4	17.5
gas No.5		gas No.8		gas No.9	
73	19.9	470	26.8	66.3	21.1
73	19.6	340	24.6	66.3	20.6
341	27.4	332	24.4	137	24.4
476	29.4	207	22.0	138	23.8
615	31.7	485	26.7	229	25
232	25.4	67	15.4	342	27.3
137	23	615	28.9	476	29.3
				624	31.8
				484	29.9
				235	25.1
				138	24.5
				104	22.1

For system (b), containing 3.5 and 5.5% C_3H_8, the equilibrium P–t values were found in the temperature range 17.2–31.0°C and pressures from 68 to 680 atm.

System (c), containing 1.4 and 4.6% iso-C_4H_{10} was investigated at 15.5–32.2°C and pressures 68–680 atm. The same authors found that the equilibrium P–t values for the CH_4 + n-C_4H_{10} system (with 0.5, 2.0, and 5.3% n-C_4H_{10}) agree, within the limits of error of the experiment with the P–t values of pure CH_4.

Experimental P–t data for mixtures (d) and (e) are given in Deaton and Frost's monograph[5]. They studied the $CH_4 + C_3H_8$ system at temperatures from 0° to + 6°C and pressures from 1 to 50 atm and the $CH_4 + C_2H_6$ system at temperatures from 2° to 10°C and pressures from 2 to 60 atm.

The experimental P–t data of McLeod and Campbell for mixtures (a) (gases Nos. 2 and 3), (b) (gas No. 5), and (c) (gases Nos. 8 and 9) are given in Table 15.

Carson and Katz[107] obtained equilibrium P–t data for the four-phase, three-component system $CH_4 + C_3H_{8\,liquid} + C_3H_{8\,gas} + H_2O_{liquid}$ in the temperature range 12.3–22.5°C and pressures from 12 to 71.5 atm. Their results are given in Table 16.

Table 16.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
22.5	71.5	12.8	15.6
20.9	52.6	16.6	27.7
18.6	35.4	18	34.5
16.6	27.4	21	56.5
14.7	21.0	20.4	50.9
18.5	36.3	21.8	53.6
10.6	12.0	13.6	17.4
17 8	32.5	12.2	17.8
10.8	12.7		

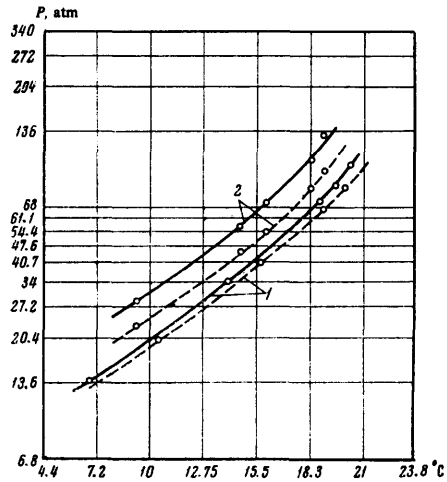

Figure 7. Conditions of formation of hydrates in mixtures containing CH_4, C_2H_4, and C_3H_6:
1) CH_4 0.326, C_2H_4 0.606, C_3H_6 0.068; *2*) CH_4 0.604, C_2H_4 0.347, C_3H_6 0.049. Continuous curves: experimental; broken lines: predicted.

Hydrates Formed by Alkane–Alkene Mixtures

Hydrate formation in the binary systems (a) $CH_4 + C_2H_4$, (b) $CH_4 + C_3H_6$, and (c) $C_3H_6 + C_3H_8$ were studied by Snell and coworkers[78] (a), Otto and Robinson[108] (b), and also Reamer and coworkers[76], Teodorovich[80], and Byk and coworkers[82] (c).

For system (a) with from 1.9 to 92.4% C_2H_4 equilibrium P–t data were obtained in the temperature range from 1.1° to 21.0°C and pressures up to 600 atm. Some P–t values were also obtained[82] for the ternary system with CH_4 32.6, C_2H_4 60.6, C_3H_6 6.8% (Fig. 7).

System (b) with from 0.5 to 23.0% C_3H_6, was studied at pressures up to 130 atm in the temperature range from 0° to 21.1°C (Fig. 8).

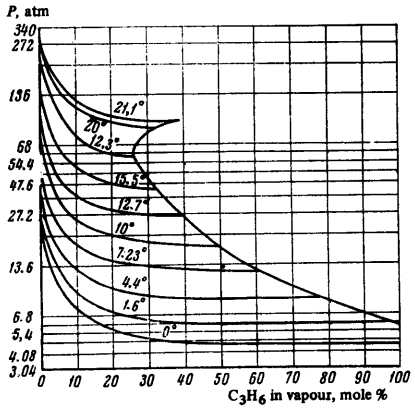

Figure 8. Effect of composition on the conditions of formation of a mixed hydrate containing CH_4 and C_3H_6.

The conditions of hydrate formation in system (c) were studied[76] for two propane–propene mixtures of different composition ($C = 0.3148$ and $C = 0.5246$, where

$$C = \frac{X_{C_3H_6}}{X_{C_3H_6} + X_{C_3H_8}},$$

at pressures from 2.9 to 26 atm (including the range of existence of a liquid hydrocarbon phase) and temperatures from 0.55° to 3.8°C (Table 17). Teodorovich[80] concluded, on the basis of the P–t values they obtained, that propene does not enter into the composition of the hydrate (contrary to the results of other authors). Byk and coworkers[82] obtained equilibrium P–t data for two gaseous mixtures which are characterised by the ratio $X_{C_3H_6}/X_{C_3H_8} = 2.87$ and 0.67. The experimental results relating to this system are given in Table 18.

Table 17.

t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
$C = 0.5246$			
0.55	2.96	3.50	7.94
1.27	3.49	3.50	8.11
1.16	3.65	3.56	9.36
1.22	3.66	3.56	12.46
1.44	3.92	3.78	18.00
2.00	4.27	3.78	18.82
1.83	4.44	3.78	19.61
1.83	4.52	3.84	27,00
3.00	4.92		
2.78	4.95	$C = 0.3148$	
2.44	4.95	0.67	3.88
2.94	4.98	1.33	4.39
3.50	6.68	1.89	4.90
		2.00	5.05
		2.06	5.26

Double Hydrates Formed by Methane with Carbon Dioxide, Nitrogen, and Argon

Unruch and Katz[91] studied the conditions of hydrate formation in the $CH_4 + CO_2$ system. They obtained P–t equilibrium data for pressures from 27 to 68 atm and temperatures from 1.1° to 11.0°C.

The $CH_4 + N_2$ system was studied by Ichaveri and Robinson[109], who experimentally determined P–t values for mixtures with various N_2 concentrations from 18 to 90% at temperatures from 0° to 22°C and pressures up to 350 atm.

Table 18.

$C = 2.87$		$C = 0.67$	
t_{equil}, °C	P_{equil}, atm	t_{equil}, °C	P_{equil}, atm
0	3.4	0.2	2.4
0.1	3.5	1.1	2.75
0.5	3.75	1.5	3
1	4.2	1.9	3.05
1.85	4.93	2.15	3.24
2.2	5.05	2.2	3.57
2.5	5.35	3.3	4.21
		3.4	4.25
		4.2	5.18
		4.3	5.21
		4.35	5.24

Equilibrium P–t values for the systems: (1) $CH_4 + Ar$ and (2) $Ar + N_2$ were obtained experimentally by Saito and Kobayashi[34] in a specially constructed apparatus by the "pressure jump" method. System (1) was investigated at temperatures from 2.7° to 25.7°C and pressures from 56 to 1120 atm; system (2) at temperatures from 2.2° to 17°C and pressures from 142 to 605 atm.

Mixed Hydrates Formed by Inert Gases

Hydrates formed by molecules of inert gas (Ar, Kr, Xe) with molecules of organic liquids (acetone, methylene, dichloride, chloroform, carbon tetrachloride) were first obtained by Waller[97]. With ideal filling of all the cavities of structure (II) these hydrates can be characterised by the general formula $A.2B.17H_2O$, where A is the organic component and B the inert gas.

Table 19.

Gas	Temperature, °C, at which P_{diss} of the mixed hydrate equals 1 atm			
	organic liquid			
	acetone	methylene dichloride	chloroform	carbon tetrachloride
Ar	−8.0	−7.0	− 4.8	− 1.6
Kr	−5.0	+6.2	+ 9.0	+11.3
Xe	+3.0	+8.6	+10.9	+13.7

As was shown by Waller, argon forms hydrates of the above type at pressures of 200–400 atm, krypton at $P \simeq$ 30 atm, and xenon at $P \simeq 1$ atm. Table 19 shows the relative stability of the $A.2B.17H_2O$ hydrates.

From Table 19, xenon gives the most stable hydrates with organic solvents. These hydrates could be obtained by simply bubbling the moist gas through the organic liquid at $P = 1$ atm and $t \sim 0$°C. Waller also states that O_2 forms mixed hydrates with acetone and N_2 with acetone and carbon tetrachloride.

Mixed Hydrates Formed by Organic Liquids

Binary hydrates A.B.17H_2O, where A and B are organic liquids (for example, A = C_2H_5Cl, B = CH_3CHCl_2, or A = C_2H_5Cl, B = $CHCl_3$ were studied by Stackelberg and Meinhold[11].

A large group of mixed (binary) hydrates formed by chloroform (or methyl iodide) with such gases as H_2, Ne, N_2, Ar, O_2, CH_4, Kr, Xe, C_2H_4, C_2H_6, and CO_2 was studied by Barrer and Ružicka[64] and is of considerable interest. Barrer and Ružicka showed that even such gases as hydrogen and neon, which themselves are incapable of hydrate formation, are retained by the small cavities of structure (II) in quantities appreciably greater (34 times for H_2 and 220 times for Ne) than in the ordinary physical dissolution of H_2 and Ne in liquid water at 0°C.

Hydrates of Multicomponent Gas Mixtures

Natural Gas

The first systematic study of the conditions of formation of hydrates was made by Hammerschmidt[4], who showed that the so-called "freezing" of gas pipes, in which natural gas is present at high ($P \gg 1$ atm) pressures and temperature $\simeq$ 0°C, is connected with the formation of solid crystalline hydrate "plugs". The natural gas investigated by Hammerschmidt had the composition (vol.%): CH_4 82.5, C_2H_6 5.99, C_3H_8 3.26, n-C_4H_{10} 0.49, iso-C_4H_{10} 0.30, CO_2 0.20, C_5 0.07, N_2 (residue) 7.19.

On the basis of their treatment of the experimental P–t values they obtained the relation: $y = 8.9(x)^{0.285}$, where y is in °F and x in lbf dm^{-2}.

In the same work, as stated above, the general premises of the hydrate formation process (thermodynamic, hydrodynamic, etc.) were examined. After the appearance of Hammerschmidt's work, which in application to natural gas can be considered classical, a large number of papers were published by foreign and Russian investigators devoted to various aspects of hydrate formation in natural gas. Carson and Katz[73] [? wrong ref. (Ed. of Translation)] studied the relation between the conditions of formation of hydrates of natural gas and its density (actual composition). They showed that an increase in the concentration of the C_2 and C_3 hydrocarbons in the natural gas appreciably raises (at constant pressure) the temperature of hydrate formation or lowers the pressure of hydrate formation (at t = const). The same problem was dealt with in a paper by Katz[110] who had studied various specimens of natural gas, the density of which varied between broad limits (from 0.55 to 1.0). Fig. 9 shows the influence of the density of natural gas on the equilibrium P–t values.

The presence in the natural gas of the impurities N_2, CO_2, and H_2S appreciably raises the temperature of hydrate formation (Fig. 10 shows the effect of N_2).

The presence of H_2S is especially effective on the equilibrium P–t values, as was shown by Molinero[111].

Campbell and McLeod[71] studied the conditions of formation of hydrates of natural gas at high pressures (up to 700 atm). Among the Russian investigations devoted to the hydrates of natural gas, the series of papers by Trebin and Makogon stand in the forefront[112–117].

Of this series of papers the investigation dealing with the problem of the formation and decomposition of hydrates of natural gas at negative temperatures[115] is of considerable interest. Trebin and Makogon showed that at the time of decomposition of the hydrate at $t < 0$°C (by reducing the pressure) there is a rearrangement of the crystal lattice of the hydrate into the ice lattice according to the scheme: hydrate → water → ice.

On passage of the hydrate from the region of positive into that of negative temperatures, the rearrangement of the hydrate lattice does not take place. In the above papers detailed consideration is given to the methods of calculation and application of appropriate nomograms which allow the conditions and place of formation of hydrates in pipelines to be determined.

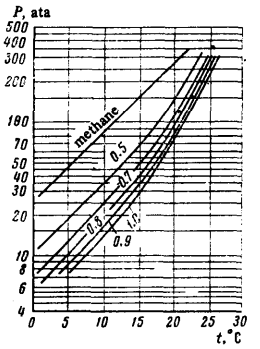

Figure 9. Conditions of hydrate formation for natural gases of various densities relative to air.

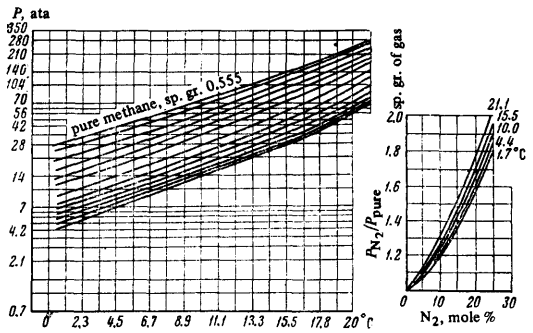

Figure 10. Conditions of hydrate formation in the presence of nitrogen in natural gas. Density of gas (from top to bottom): *1*) pure methane 0.555; *2*) 0.56; *3*) 0.57; *4*) 0.58; *5*) 0.59; *6*) 0.60; *7*) 0.62; *8*) 0.64; *9*) 0.66; *10*) 0.68; *11*) 0.70; *12*) 0.80; *13*) 0.90.

The influence of stabilising gases was considered simultaneously[115].

Ponomarev's studies[118,119] examined the problem of the formation of hydrates of natural gas of different composition, and also commercial gases containing a relatively large proportion of propane. For natural gas, Ponomarev obtained numerical values of the constants K and B in equations of the type $t = K \lg P - B$ where t and P are respectively the temperature and pressure of hydrate formation.

Khoroshilov[120–122] gives methods of calculating the equilibrium parameters of hydrate formation for natural gas.

Liquefied Hydrocarbon Gases

Hydrate formation in mixtures of liquid hydrocarbon gases (C_3H_8 + n-C_4H_{10}) has been considered by Musaev[123-125].

The same author investigated the hydrate formed by the liquid products of the thermal treatment of petroleum, having the following fractional composition (wt.%) C_2 4.3, C_3 16.9, iso-C_4 8.2, n-C_4 18, iso-C_5 18.4, n-C_5 17.0, C_6 17.3. Musaev's conclusions concerning the influence of n-C_4H_{10} on hydrate formation in C_3H_8 + n-C_4H_{10} mixture and also the influence of the rate of cooling on the temperature of formation of the hydrate of liquid propane are interesting. According to Musaev, n-C_4H_{10} does not participate in the hydrate formation.

Hydrocarbon Mixtures Formed in the Pyrolysis of Petroleum Products

The conditions of formation of hydrates of pyrogas were studied by Byk[126]. The material selected for investigation was an industrial gas from the pyrolysis of benzines of the following composition (vol.%): H_2 14.8, CH_4 45.1, C_2H_4 21.9, C_2H_6 10.0, C_3H_6 5.3, C_3H_8 0.9, ΣC_4, C_5 5.0. For two pressure ranges (20–35 and 35–50 atm) empirical equations connecting the temperature of hydrate formation (°C) and the corresponding equilibrium pressure (atm) were obtained: (1) $t = 0.27P + 2.4$, and (2) $t = 0.105 P + 8.5$.

IX. CALCULATION OF THE CONDITIONS OF HYDRATE FORMATION AND OF THE COMPOSITIONS OF THE SOLID (HYDRATE) AND GAS PHASES

As already stated above, mixed hydrates formed by binary and multicomponent mixtures are now considered to be solid solutions, the composition of which varies during the decomposition of the hydrate. On the basis of the analogy between the solid and liquid solutions (from the standpoint of the gas or vapour phase found in equilibrium with them) Wilcox and coworkers[79] proposed a method of calculating the conditions for the formation of hydrates from gas mixtures. The method is based on the use of numerical values of the "equilibrium constant" $K_{v/s} = y_i/x_i$ where y_i is the mole fraction of component i in the gas (vapour) phase, and x_i the mole fraction of the same component in the solid hydrate phase. The value of $K_{v/s}$, just as for liquid solutions, depends on the temperature, pressure, and composition of the mixture. The conditions of formation of a mixed hydrate from an i-component gas mixture is determined by the equality:

$$\sum_{i=1}^{i=n} \frac{y_i}{K_{v/s}} = \sum_{i=1}^{i=n} x_i = 1.$$

Hence when the nature of the dependence $K = f(t, P)$ is known for all the components of a gas mixture (the authors considered natural gas), then by carrying out the simplest linear interpolation the temperature at which the condition $\sum_{i=1}^{i=n} x_i = 1$ is observed for a given pressure can be determined (or, on the other hand, for a specified temperature the corresponding equilibrium pressure can be calculated).

This method was developed further in a series of later papers by Carson and Katz[107,127,128], who constructed $K_{v/s} = f(P)$ and $K_{v/s} = f(t)$ diagrams for the individual components of natural gas: methane, ethane, propane, and isobutane. In constructing such diagrams naturally it is necessary to locate experimental data on the compositions of coexisting solid (hydrate) and gas phases.

These results were taken from Hammerschmidt's work[4] (gas phase: natural gas at a pressure of 41 atm, Table 20) and from the publications of Deaton and Frost[83], who studied the compositions of the coexisting phases in the systems: (1) $CH_4 + C_2H_6$, (2) $CH_4 + C_3H_8$, and (3) CH_4 + iso-C_4H_{10}. For natural gas containing hydrogen sulphide and carbon dioxide as impurities in order to carry out calculations by the method of Wilcox and coworkers it is necessary to allow for the values of $K_{v/s}$ for H_2S and CO_2.

Table 20.

Component	Composition of gas phase, vol. %	Composition of hydrate, vol. %
CH_4	82.5	56.95
C_2H_6	5.99	5.66
C_3H_8	3.26	24.97
iso-C_4H_{10}	0.30	4.69
n-C_4H_{10}	0.49	0.83
C_5H_{12}	0.07	0.00
CO_2	0.20	0.44
N_2	7.19	0.46

The nature of the dependence $K_{v/s} = f(P, t)$ for these two gases was investigated by Noaker and Katz[106] (H_2S + CH_4 system) and by Unruch and Katz[91] (CO_2 + CH_4 system). A handbook[65] edited by Katz gives $K = f(P, t)$ diagrams for CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, CO_2, and H_2S.

It should be noted that on all these diagrams the maximal pressure is ~ 280 atm. Consequently the conditions of hydrate formation for mixtures of the natural gas type can be calculated by the method of Wilcox and coworkers only at $P_{dis} \leq 280$ atm.

In this connection the work of McLeod and Campbell[71] is interesting; they proposed a method for calculating the temperature of hydrate formation of natural gas in the pressure range 400–680 atm.

The authors, using a modernised form of the Clausius–Clapeyron equation $d \ln P/dT = m$, obtained in the general form the equation $C = mT^2$, where $C = \Delta H/zR$.

Having found that in C_1–C_4 alkane mixtures (not containing n-C_4H_{10}) in the pressure range 400–680 atm, m = const = 0.066, McLeod and Campbell obtained the formula $C = 0.066T^2$, in which the temperature is expressed in degrees Rankine.

To calculate the hydrate formation temperature the value of C for the specified pressure must be found by using the additivity rule ($\sum_{i=1}^{i=n} C_i = C$). Naturally, in making such calculations it is necessary to know the value of C for each hydrocarbon at various pressures. These values were obtained by McLeod and Campbell experimentally for methane ethane, propane, and isobutane and given in the form of Tables[7].

It should be noted that the number of papers in which the information given about the composition of the coexisting solid (hydrate) and gas phases was found directly by experiment is comparatively small.

Apart from those mentioned above, they include:

1. An investigation by Otto and Robinson[108], who determined the compositions of the equilibrium phases in the

$CH_4 + C_3H_8$ system in the temperature range from 0°to21°C and pressures from 7 to 204 atm.

2. An investigation of the compositions of the coexisting phases in the system $CH_4 + C_2H_4$ made at temperatures from 0° to 29°C and pressures from 6.8 to 612 atm by Snell and coworkers[78].

3. Equilibrium compositions in the $C_3H_8 + C_3H_8$ system‡, determined at 0.3°C by Fomina and Byk[129] and presented as a P–X diagram in Fig. 11.

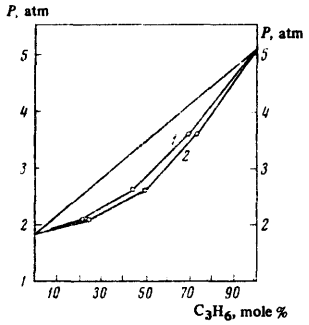

Figure 11. P–X isothermal equilibrium diagram for the C_3H_6–C_3H_8–H_2O system.
1) Hydrate; *2*) gas.

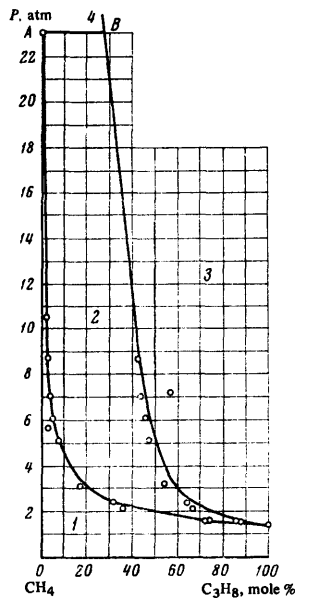

Figure 12. P–X isothermal equilibrium diagram for the C_3H_8–CH_4–H_2O diagram.
1) Gas-ice; *2*) hydrate-gas-ice; *3*) hydrate-ice; *4*) hydrate$_I$–hydrate$_{II}$-ice.

‡ The first attempts to determine the compositons of the equilibrium phases in the $C_3H_6 + C_3H_8$ system was made by Reamer[76] but the relative volatilities (α) found were almost equal to 1.

4. The same authors[130] determined, at 0.65° and 1.2°C, the compositions of the coexisting phases in two systems containing 2-methylpropene:

(a) $C_3H_8 + i\text{-}C_4H_{10} + i\text{-}C_4H_8$;

(b) $C_3H_8 + i\text{-}C_4H_{10} + i\text{-}C_4H_8 + C_3H_6$.

During the investigations a mixed hydrate was obtained which contained up to 82.5 vol.% 2-methylpropene and by extrapolation for the temperature range 0.66–1.2°C the equation $\lg P = 27.9298 - 7629/T$ was found, where P is the dissociation pressure of the hypothetical hydrate of pure 2-methylpropene.

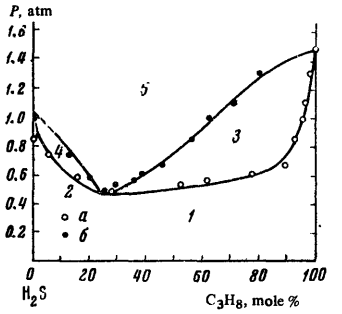

Figure 13. P–X isothermal equilibrium diagram for the H_2S–C_3H_8–H_2O system:
a) composition of gas phase; *b*) composition of hydrate.
1) Gas-ice; *2*) hydrate$_I$–gas-ice; *3*) hydrate$_{II}$–gas-ice; *4*) hydrate$_I$–gas-ice; *5*) hydrate$_{II}$–ice.

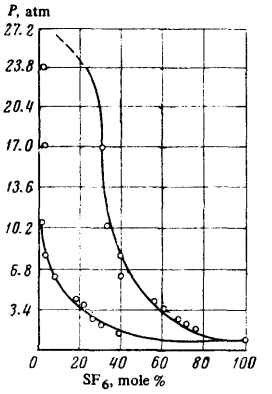

Figure 14. P–X isothermal equilibrium diagram for the CH_4–CF_6–H_2O system.
Continuous curves: experimental; points: calculated.

5. The isothermal "hydrate–gas phase" equilibrium ($t = -3$°C) in the $CH_4 + C_3H_8$ and $C_3H_8 + H_2S$ systems, including the determination was investigated by van der Waals and Platteeuw[28,29]; this involved the determination of the compositions of the coexisting phases. Figs. 12 and 13 give their P–X equilibrium diagrams they obtained. In the $C_3H_8 + H_2S$ system they observed an interesting phenomenon, analogous to anisotropy in liquid solutions: at $t = -3$°C and $P_{diss} = 0.48$ atm the compositions of the hydrate and gas phases agree (~ 75 mole % H_2S).

Hence the constancy of the value of P_{diss} for this hydrate observed by Stackelberg and Frühbuss[12] is connected with the existence of an azeotrope.

6. Ichaveri and Robinson[109] studied the compositions of the coexisting gas and hydrate phases in the $CH_4 + N_2$ system at −0.1° and 6.6°C.

In this system methane is the less volatile component ($K_{v/s} < 1$).

The compositions of the equilibrium gas and hydrate phases in the $CH_4 + SF_6$ system were studied at $t = -3$°C over the whole concentration range and pressures from 0.72 to 23.2 atm by Sortland and Robinson[36]. Fig. 14 shows their experimental results as a $P-X$ diagram.

X. USE OF THE PRINCIPLES OF STATISTICAL MECHANICS IN STUDYING GAS HYDRATES

The possibility of using the principles of statistical mechanics in studying solid non-stoichiometric clathrates, and consequently, hydrates, was shown in the studies[22-28] of Barrer, and of van der Waals (grandson) and Platteeuw. This subject is covered most fully in the monograph of the last two authors[28].

By applying the methods of statistical mechanics to a three-dimensional Langmuir model for the ideally localised adsorption of spherical molecules in the cavities of a clathrate (hydrate) lattice and by considering the hydrate phase as a solid solution obeying Raoult's law, van der Waals and Platteeuw obtained equations which allow several fundamental (principally thermodynamic) properties of gas hydrates to be calculated (dissociation pressure of the hydrates at various temperatures, their heats of formation, the compositions of the coexisting equilibrium phases, etc.). The main equations of van der Waals and Platteeuw are:

$$\text{(I)}\ \Delta\mu = kT\Sigma\nu_i \ln(1 + \Sigma C_{K_i} f_K),$$

$$\text{(II)}\ y_{K_i} = C_{K_i} f_K/(1 + \Sigma C_{K_i} f_K),$$

where $\Delta\mu = \mu^\beta - \mu^\alpha$ is the difference in chemical potentials of the empty crystal lattice of the hydrate (μ^β) and stable ice (μ^α), f_K is the fugacity of the adsorbed substance (K); v_i, the crystallographic constant of the cavities of the hydrate lattice with radius a_i, characterises the number of molecules of K per molecule of water. For structure (I), $\nu_1 = \frac{1}{23}$ and $\nu_2 = \frac{3}{23}$. For structure (II), $\nu_1 = \frac{2}{17}$ and $\nu_2 = \frac{1}{17}$. y_{Ki} is the probability of finding a molecule of gas K in a cavity of a hydrate lattice of type i, and C_{Ki} is the Langmuir constant for molecules of K in cavities i.

$$\text{(III)}\ C_{K_i} = \frac{4\pi}{kT}\int \exp[-\omega(r)/kT]\, r^2\, dr.$$

Here $\omega(r)$ is the spherical symmetrical potential of molecule K at distance r from its centre to the wall of the cavity. In the general form for a characteristic of the interaction between the cavity walls and the molecule K the authors employed the Lennard-Jones–Devonshire (12–6) potential:

$$\{\omega(r) = 4\varepsilon\{(\sigma/R)^{12} - (\sigma/R)^6\}.$$

On the basis of Eqns. (I), (II), and (III) given above, van der Waals and Platteeuw[28] calculated the dissociation pressure of a series of hydrates at 0°C (Table 21).

As Table 21 shows, good agreement between experimental and calculated values of P_{diss} is observed for hydrates of Kr and Xe (monatomic molecules) and to a lesser extent for almost spherical molecules (C_2H_4, C_2H_6).

The fundamental equations (I), (II), and (III) given above allow the composition of a solid hydrate phase in equilibrium with a gas phase to be calculated. Such calculations were made by van der Waals and Platteeuw[28,29] for the systems $CH_4 + C_3H_8 + H_2O$ and $C_3H_8 + H_2S + H_2O$ with the aid of the equations:

$$\text{(a)}\ y_{A_1} = C_{A_1} P_A/(1 + C_{A_1} P_A);\quad y_{A_2} = C_{A_2} P_A/(1 + C_{A_2} P_A),$$

$$\text{(b)}\ \nu_1 \ln(1 - y_{A_1}) + \nu_2 \ln(1 - y_{A_2}) = \frac{-\Delta\mu}{kT},$$

$$\text{(c)}\ Y_A = \nu_1 y_{A_1} + \nu_2 y_{A_2},$$

Table 21.

Hydrate-forming substance	P_{diss} at 0°C, atm	
	expt.	calc.
Ar	95.5*	95.5*
Kr	14.5	15.4
Xe	1.15	1.0
CH_4	26	19
CF_4	1	1.6
C_3H_8	5.2	1.1
C_2H_4	5.44	0.5

* The experimental value of P_{diss} for argon hydrate was used in the calculation. The constant thus found was used to calculate P_{diss} for the remaining hydrates.

where y_{A_1} is the fraction of small cavities of the hydrate lattice filled with molecules of A, y_{A_2} the fraction of large vacancies of the hydrate lattice filled with molecules of A, P_A the partial pressure of component A in the equilibrium gas phase, C_{A_1} the Langmuir constant of component A for when it fills the small vacancies, C_{A_2} that for when it fills the large vacancies, and Y_A the concentration of component A in the equilibrium hydrate.

As the authors showed, for a mixed hydrate of structure (I) $\Delta\mu = 0.167$ kcal mole^{-1} (Br_2 hydrate model). For a hydrate of structure (II), $\Delta\mu = 0.196$ kcal mole^{-1} SF_6 hydrate model). The results of the calculations for $t = -3$°C showed good agreement with experimental results, as is clear from the $P-X$ diagrams for the two systems (Figs. 12 and 13).

A theory of solid hydrate solutions using the principles of statistical mechanics has obtained its furthest development in the studies of Saito and coworkers[32,34], who somewhat modified the equations of van der Waals and Platteeuw[28] and proposed a method of calculating several properties of gas hydrates at temperatures above the lower quadruple point (in practice at $t > 0$°C). The objects of their investigations were the hydrates of methane, argon, and nitrogen, and also mixed hydrates in the $CH_4 + Ar + H_2O$ and $Ar + N_2 + H_2O$ systems. P_{diss} for the individual hydrates of CH_4, Ar, and N_2 were calculated as functions of temperature and pressure up to 3000 atm and agree well with the experimental results, the heats of formation of the hydrates, and also the number of water molecules (n).

In finding the nature of the $n = f(P)$ dependence, Saito and coworkers[32] showed that for the hydrates of Ar and N_2 complete filling of the small and large cavities of the hydrate lattice ($n = 5.75$) is attained only at very high equilibrium pressures, of the order of 3400 atm. For $CH_4 \cdot nH_2O$ complete filling is attained at $P = 1300$ atm. Their calculated values of the heats of formation of these (Ar, N_2, and CH_4) hydrates agreed well with the values obtained from $P-t$ results with the aid of the Clausius–Clapeyron equation. Saito and Kobayashi[34] calculated for $CH_4 + Ar$ and $Ar + N_2$ mixtures the conditions of hydrate formation over a wide range of temperature and pressures, which also

agreed well with those they obtained experimentally. The same authors calculated the composition of a mixed argon–methane hydrate which coexists in equilibrium with the gas phase at the temperatures 4.4°, 10.0°, 15.5°, and 21°C.

All the above-mentioned calculations of the properties of hydrates were based on the use of the Lennard-Jones–Devonshire potential, which is known not to take into consideration the form and size of the gas molecules. The first successful attempt to calculate P_{diss} of hydrates by use of the values of the Kihara potential, the value of which, in principle, depends on the form and size of the interacting molecules, was made by McLeod and McKoy and Sinanoglu[33]. The authors calculated P_{diss} for a series of hydrates by using the Lennard-Jones (28–7) potential, the Lennard-Jones (12–6) potential, and the Kihara potential. They showed that the least satisfactory agreement with the experimental results is given by using the Lennard-Jones (28–7) potential. As might be expected, the (12–6) potential gives satisfactory results for molecules of monatomic gases and CH_4 but is not very satisfactory for the molecules C_2H_6, CO_2, N_2, O_2, C_2H_4. Furthermore, the use of the Kihara potential allows sufficiently good agreement with experimental values of P_{diss} to be obtained for the above rod-shaped molecules. The Kihara potential found further use in Nagata and Kobayashi's work[35,37]. In the first of these papers, on the $CH_4 + N_2$ binary system, the hydrate formation pressure was calculated for a mixture with 55% CH_4 and also the compositions of the coexisting hydrate and gas phases in equilibrium at −0.1° and 6.6°C. Satisfactory agreement was shown with experimental P–X data published earlier[109]. In the second paper the authors calculated P_{diss} for the mixed hydrates formed in the $CH_4 + C_2H_6$ and $CH_4 + C_3H_8$ systems, using only the constants given in the literature which characterise the individual hydrates of CH_4, C_2H_6, and C_3H_8. Their results also agree well with the experimental data.

Use of statistical mechanical methods allowed Barrer and Stuart[23] and then Barrer and Ružicka[64], to make quantitative evaluations of the stabilising influence of an auxiliary gas on the hydrate formation temperature. Their approximate calculations for the mixed hydrate formed by chloroform and nitrogen showed that when the N_2 is in the small cavities of structure (II) and partly in the large cavities, then $\Delta\mu = \mu^{\beta} - \mu^{\alpha} = -115.2$ kcal mole^{-1}. In the absence of nitrogen the value is −112 kcal mole^{-1} and consequently the difference is 3.2 kcal mole^{-1} and is due to the effect of the rise in the $CHCl_3$ hydrate formation temperature in the presence of nitrogen.

XI. PHYSICAL KINETICS OF THE FORMATION OF HYDRATES

The problem of the dependence of the rate of formation of gas hydrates on various factors in one form or another is treated in many papers devoted to the determination of their formation conditions. They include the investigations of Hammerschmidt[4], Ceccoti[55], Tesner and co-workers[131], Musaev[125], etc. Indications of the promoting action of certain additions (which by themselves do not enter into the composition of the hydrate) are contained in the work of van der Waals and Platteeuw[28] and also van Cleef and Diepen[31]. We know of only five studies specially devoted to the physical kinetics of hydrate formation, and with the exception of one[132] which examined the kinetics of hydrate formation, they all deal solely with the hydrates of organic liquids, and the conclusions drawn in these papers cannot, according to the authors's own statements, be extended to purely gas hydrates. Pinder[100] studied the dependence of the rate of formation of tetrahydrofuran hydrate $[CH_2]_4O.17H_2O$ on the processes of mutual diffusion of the two complexes with a hydrogen bond which exist in the initial solution. Keneth and Pinder[133] investigated the rheological properties of the hydrate system of tetrahydrofuran + hydrogen sulphide. The hydrate they investigated exhibits high stability (at $P = 1$ atm, $THF.2H_2S.17H_2O$ is destroyed at $t > 21$°C). They also studied the viscosity of hydrate *slush* at a function of time, rate of growth of individual crystals, etc.

Saito and Sadanaga[134] studied the process of formation of the hydrate of dichloromonofluoromethane ($CHCl_2F.17H_2O$) and obtained a series of empirical equations connecting the rate of formation of crystalline hydrate nuclei with the degree of supercooling of the solution and the number of revolutions of the stirrer.

The most fundamental investigation on the physical kinetics of the hydrate formation process is, perhaps, the work by Barrer and Ružicka[135]. They measured the rate of formation of binary hydrates produced by chloriform or THF with Ar, Kr, Xe, and CH_4, at various temperatures (−78° and ~ 0°C).

Their method of investigation (measurements of the quantity of gas absorbed after definite intervals of time) allowed them to obtain at constant P, t a series of single-valued curves (almost straight lines) which characterise the rate of formation of the hydrates mentioned above. With the binary hydrate of THF + argon as example, these authors also examined in detail the factors which determine the growth of the crystallisation nuclei in the formation of the hydrate.

XII. DENSITY OF HYDRATE CRYSTALS

The density of the crystals of the hydrates was first measured by Stackelberg[7,11] for the following organic compounds (Table 22).

Table 22.

Hydrate	Density, g cm^{-3}
SO_2	1.23
$CHCl_3$	1.11
C_2H_5Cl	<1.0
$CCl_4 + H_2S$	1.272±0.01
$CHCl_3 + H_2S$	1.216±0.01
Cl_2*	1.29±0.1

* Calculated from the slope of the curve (dT/dP).

Precision measurements of the density of hydrate crystals were made by Saito and Sadanaga[136]. In a specially equipped room with a temperature of 0°C they used a float method to measure the density of hydrates of propane and also of several chlorofluoro-derivatives of methane (CHF_2Cl, $CHFCl_2$, CF_2Cl_2, and $CFCl_3$).

From propane hydrate, $d = 0.88$ g cm^{-3}; for the hydrates of the above chlorofluoromethanes, the density lay within the limits 1.04–1.24 g cm^{-3}.

Saito and Sadanaga also proposed formulae for calculating the density of hydrates of structures (I) and (II):

$$d_I = \frac{(46\,H_2O + 6\,M\cdot\alpha_1)\,1/N}{a^3}; \quad d_{II} = \frac{(136\,H_2O + M\cdot\alpha_2)\,1/N}{a^3}$$

where M is the molecular weight of the hydrate-forming substance, α_1 and α_2 are the degree of filling of the cavities in the crystal lattice of the hydrate ($1 \geqslant \alpha > 0$), N is Avogadro's number, and a the crystal lattice parameter of the hydrate, Å. They found good agreement between experimental and calculated values of the density of the hydrates mentioned.

Van Cleef and Diepen[31] give the values of the densities they found for the hydrates of oxygen ($d = 1.03 \pm 0.02$ g cm^{-3}) and nitrogen ($d = 1.02 \pm 0.02$ g cm^{-3}).

XIII. INDUSTRIAL USE OF GAS HYDRATES

1. DESALINATION OF SEA WATER

A process first proposed by Donath[137] for the desalination of sea water is based on the use of hydrocarbon hydrates (of ethane, propane, and isobutane), and also of hydrates formed by halogen derivatives of methane, mainly the Freons and certain other gases (Cl_2).

The paper by Kuoch and coworkers[138] gives the principles of the method in greatest detail, and also the technological scheme of the process, based on the formation and subsequent decomposition of propane hydrate.

According to the scheme given, the hydrate ($C_3H_8.17H_2O$) is made in a special reactor at 1.1°C and a pressure of 3.9 atm. In a second reactor, into which the hydrate mud is brought by means of a conveyor belt, the hydrate is decomposed at 7.2°C and 4.7 atm, with the liberation of pure distilled water (the salt dissolved in sea water is known not to permeate the hydrate lattice). In this way, 40% of the sea water put into the first reactor was desalinated.

The process for the desalination of sea water with the aid of hydrates is covered by a series of foreign patents[139,140] and also by papers of Caryofcky[141], Barduhn[142], and Medvedev[143].

2. USE OF HYDRATES FOR THE STORAGE OF GASES

The storage of natural gas as hydrates is considered in several patents and publications[48,49,144]. Mock[145] has proposed an interesting method for the storage of inert gases (Ar, Kr, Xe).

3. SEPARATION OF GASEOUS AND LIQUID MIXTURES WITH THE AID OF HYDRATES

The separation of these mixtures with the aid of hydrates has been considered in detail in a paper by Barrer and Ružicka[64] which gives the principles of the method and considers some specific separable gaseous and liquid mixtures ($O_2 + N_2$, Kr + Ar, Xe + Kr, $CH_3I + CHCl_3$, $C_6H_5CH_3 + CHCl_3$, $C_6H_6 + CHCl_3$, $CH_2Cl_2 + CHCl_3$). These problems are also covered in the patent literature. Thus, Crowther[146] proposed a method of separating the gaseous mixture $CH_4 + C_2H_6$. Glew's patent[147] deals with the separation by hydrate formation of the liquid hydrocarbon mixture $C_3H_6 + C_3H_8$. Kinney and Kahre[148] proposed a method of separating helium from natural gas. The patent proposes that in the last stage of the process an N_2 + He mixture is separated by adding propane, which forms a mixed hydrate with the nitrogen. Byk and Fomina's patent[149] covers the separation of the gaseous mixtures n-C_4H_{10} + iso-C_4H_{10}, and $C_3H_6 + C_3H_8$.

XIV. PREVENTION OF HYDRATE FORMATION

Methods for preventing hydrate formation derive directly from the equilibrium conditions for their existence given above (P_{gas}, P_{H_2O}, and t°C): (1) raising the temperature in the system where a hydrate has already formed or can be formed; (2) reducing the pressure of the hydrate-forming gas; (3) reducing the concentration of water in the gas by drying it or by using special inhibitors which lower the partial pressure of water vapour in the system.

Detailed consideration of all the methods for preventing hydrate formation has been given in the extensive Russian and foreign literature on the subject, dealing mainly with the problems of the drying of gases[150-155] and the use of various inhibitors[117,156-174].

Measures against hydrate formation are considered in the Russian monographs by Sarkis'yants and Makagon[175,176], and also in Frost and Deaton's monograph[5].

The theoretical principles of the inhibition of hydrate formation, which are of independent interest, and also the specific possibility of using individual inhibitors (methanol, ethanol, isopropyl alcohol, glycine solutions, propanol, aqueous solutions of $CaCl_2$, NaCl, LiCl, $AlCl_3$, NH_3, etc.) have been considered[177-180].

The most complete theory of the inhibiting action of a "third" component has been given by Pieroen[180], who by using the concepts of the chemical potentials of the components, participating in the hydrate formation, and of the "activities" of the aqueous solutions obtained the equation

$$\Delta T = -\frac{nRT_0^2}{\Delta H} X_{t.c.},$$

in which ΔH is the heat of formation of one mole of hydrate containing n moles water at T_0; $\Delta T = T_0 - T$; T_0 is the equilibrium temperature (°K) of formation of the hydrate in the absence of inhibitor; T that in the presence of the inhibitor; and $X_{t.c.}$ the mole fraction of the inhibiting third component in the water. For the natural gas–water system, the above equation acquires the form:

$$\Delta T = \frac{nRT_0^2}{\Delta H} \frac{18\omega}{(100-\omega)M} (1 - X_{t.c.}),$$

since $X_{t.c.} \ll 1$, then

$$\Delta T \sim \frac{nRT_0^2}{\Delta H} \frac{18\omega}{(100-\omega)M},$$

where w is the inhibitor concentration (wt.%) in the water, M the molecular weight of the inhibitor at $T = 280$°K, and $\Delta H \simeq -41$ kcal mole^{-1}, so that

$$\Delta T \sim 1240 \frac{\omega}{M(100-\omega)}.$$

Earlier[178], Hammerschmidt obtained an analogous formula with the numerical coefficient equal to 1297 for inhibiting aqueous solutions of electrolytes.

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Synthesis of Technical Tanning Agents

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The review gives data mainly on Soviet investigations on the preparation and application of synthetic tanning agents, comprising auxiliary syntans and substitutes for vegetable tannins. A detailed account is given of the processes used in the synthesis of Soviet heavy-duty syntans and some information on the production of substitute syntans abroad. The bibliography contains 83 references.

CONTENTS

I. Introduction 491
II. Auxiliary syntans 492
A. Auxiliary syntans for use with vegetable tanning agents 492
B. Auxiliary syntans for special purposes 493
III. Syntans used as substitutes for vegetable tannins 495
A. Development of methods for the production of substitute syntans in the USSR 495
B. Processes employed in the synthesis of Soviet heavy-duty syntans 496
C. Methods of producing substitute syntans abroad 498
IV. New types of synthetic tanning agents 500

I. INTRODUCTION

Since the earliest times tanning agents, found in the bark, wood, leaves, and roots of various plants, have been used for the production of leather. The structure of these substances, which are known generally as "tannins", was elucidated as a result of the large amount of work done during the second half of the nineteenth century and the beginning of the twentieth century. All natural tanning agents are derivatives of polyhydric phenols, and are divided into two groups: the chief structural unit of hydrolysable tannins is digallic acid, which forms esters with hexoses; non-hydrolysable tannins are based on catechol units linked together either directly or through carbon atoms [1].

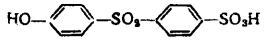
At the same time as the investigation of the structure of vegetable tannins, and directly connected with it, work was also done on the synthesis of tanning agents with the above main structural units as starting materials. Such syntheses were undertaken by Schiff, Baeyer, Fischer, Melau, and others, who by various methods obtained condensation products of arenepolyols and hydroxybenzoic acids.

The work of Schiff is of especial interest for the history of synthetic tanning agents. Having obtained digallic acid from gallic acid by the action of phosphoryl chloride, he applied this method to pyrogalloisulphonic acid and hydroxybenzenesulphonic acid [2], and assigned to the products the formulae

$$C_6H_2(OH)_3—SO_2—O—C_6H_2(OH)_2—SO_3H,$$
$$C_6H_4(OH)—SO_2—O—C_6H_4—SO_3H.$$

While differing from digallic acid in composition, these compounds showed some analogy with it in molecular structure: they contained phenolic rings linked by ester groups (-CO.O- or $-SO_2.O-$) and one of the rings contained an acidic group (-COOH or $-SO_3H$). Both compounds possessed tanning properties, and underwent all the reactions characteristic of vegetable tannins.

Schiff also obtained a tanning agent [3], probably hydroxyphenylsulphonylbenzenesulphonic acid



by dehydrating hydroxybenzenesulphonic acid at a high temperature.

These compounds obtained by Schiff must be regarded as direct precursors of modern synthetic tanning agents.

The history of modern industrial synthetic tanning agents, usually termed syntans (synthetic tannins), began in 1911, when Stiasny made a patent application covering the production of tanning materials by the condensation of hydroxybenzenesulphonic acids with formaldehyde [4,5]. Synthetic tanning agents have come a long way. More than a thousand patents have been issued on processes for their production, while the total number of brands manufactured in various countries reaches two hundred.

Synthetic tanning agents can be divided into two main groups—"light" and "heavy"—from the point of view of leather technology. Those of the first group possess weak

forming and filling power. They do not confer the required commercial properties on leather, but their use together with vegetable extracts or mineral salts has a substantial effect on the tanning process and on the properties of the leather. In conformity with this they are usually termed auxiliary.

Synthetic tanning agents of the second group approach vegetable tannins in their tanning action, and several of them even surpass the latter. Therefore the "heavy" syntans can replace vegetable extracts either completely or to a considerable extent. Hence the name substitute syntans.

Only very few synthetic tanning agents are individual compounds. Most of them are polydisperse mixtures of oligomers. Their tanning ability depends both on the chemical type and on the physicochemical characteristics of the product (degree of polycondensation, degree of dispersion). The range of possible variation in physicochemical characteristics differs in different chemical types, so that the range of technical properties with respect to leather (tanning action) which is possible for them also differs. From sulphonic acids of aromatic hydrocarbons, for example, only auxiliary tanning agents can be obtained, whereas hydroxybenzenesulphonic acids enable syntans to be prepared with any properties–from light auxiliaries to complete substitutes.

II. AUXILIARY SYNTANS

The group of auxiliary synthetic tanning agents was the first to appear, remained the only group for twenty years, and until now has been the most widely used in foreign countries.

Brands belonging to this group are used for two main purposes: (1) they are combined with vegetable extracts to improve the dissolution of the latter, accelerate tanning, lighten the leather, and protect the tanning solutions from fermentation and putrefying processes, the partial replacement of vegetable tannings being of second importance; and (2) they are combined with a mineral tannage (mainly chrome) to thicken the leather, enhance the plasticity of the fare side, bleach the skin, and prepare it for dyeing and finishing operations.

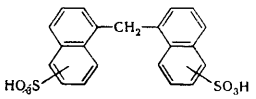
A. Auxiliary Syntans for Use with Vegetable Tanning Agents

This category was first realised in production as the synthetic tanning agent Neradol D, manufactured by the Badische Anilin- und Sodafabrik in conformity with Stiasny's patent. The idea underlying the process was that, in order to obtain an economically acceptable product, possessing the three main chemical and physicochemical characteristics of vegetable tannins–phenolic nature, a large molecule and solubility in water–the most accessible starting material was phenol and its homogues, the molecule was enlarged by condensation with formaldehyde, and solubility could be ensured by introducing a sulpho-group.

Neradol D was dihydroxydiphenylmethanedisulphonic acid. It precipitated gelatin from solution, and showed some resemblance to vegetable tannins in its qualitative reactions, but it differed sharply from them in its tanning power. It was not an analogue of vegetable tannins, but a representative of a new type of tanning material, giving a special kind of leather–light, smooth, and not compact–unsuitable for those purposes for which vegetable-tanned leather is used. Without being a complete substitute, Neradol D was, however, useful for combining with vegetable extracts: it lightened the leather, and prevented the formation of precipitates in the tanning solutions, which economised the consumption of tannins.

The industrial realisation of Stiasny's patent stimulated the development of analogous processes for obtaining tanning agents, and during the following years it was established that the presence of a hydroxy-group was not necessary for an aromatic sulphonic acid to exert a tanning action, this being possessed also by sulphonic acids of hydrocarbons and of certain heterocyclic compounds.

The first patent on syntans from hydrocarbons was issued[6] in 1916. The product was a mixture of naphthalene-1- and -2-sulphonic acids condensed with formaldehyde



and was named Neradol ND. The naphthalene syntan possessed poorer tanning power than the phenol syntan, but differed little from it in the effect achieved on being combined with vegetable extracts.

Neradol ND was succeeded by Ordoval, a product resulting from the sulphonation of mixtures of carbazole and anthracene, crude anthracene, or "anthracene residues".[7] This syntan, in contrast to the Neradols, possessed no brightening power, but in its tanning action even somewhat surpassed Neradol ND.

The absence of special advantages in the phenolic syntan and its relative dearness pushed it into the background.

The blockade of Germany during the First World War led to a shortage of tanning materials, and at first syntans were widely used to replace them. The large-scale application of syntans and the ignorance of their specific features and differences from natural tannins resulted in wholesale damage to leather, caused by the hydrolysis of collagen. The consequences of this were very unfavourable for syntans. By 1923 the manufacture of Neradols and Ordoval had fallen to a very low level. The use of artifical tanning materials as replacements for vegetable tannins almost ceased in the West for more than a decade[8].

During this period, in which interest in synthetic tanning agents dropped sharply in the West, the present Reviewer together with Kiprianov and Tolkachev began investigations in this field at the Ukrainian Institute of Applied Chemistry in Kharkov. At that time a large quantity of tanning extracts were imported into the USSR from abroad, and therefore even a partial replacement of vegetable by artificial tanning agents would have been of great economic value. In addition, the industrial manufacture then of new chemical products involved serious difficulties, and the contingency depended on the choice of raw material and the necessary equipment. The German commercial brands were soon identified and data were obtained which might serve as a control in our experiments[9].

Crude anthracene– a technical mixture of polycyclic aromatic hydrocarbons and heterocyclic compounds, which is precipitated from anthracene oil on cooling–was selected as the most accessible starting material. The composition of crude anthracene is variable: the solid part constitutes ~70%, and contains on the average 60% of phenanthrene, 20% of carbazole, and 15% of anthracene[10]. The first two components are of great value for the production of tanning materials. They are considerably more readily sulphonated, and give clearer solutions. Increasing the content of anthracene in the mixture makes it difficult to

obtain a product of satisfactory quality. Enriched anthracene must be regarded as, in general, unsuitable for the synthesis of tanning agents.

Crude anthracene was sulphonated with 150% of 92% sulphuric acid at 120°C for 5 h, with formation of a mixture of sulphonic acids of equivalent weight 210–220, which corresponds approximately to equal proportions of mono- and di-sulphonic acids. Sulphonation is accompanied by some resinification of the product with liberation of sulphur dioxide. The addition of a small amount of naphthalene helped to stabilise the solution [11]. Condensation of the sulphonated mass with formaldehyde, which is necessary with hydroxybenzene- and naphthalene-sulphonic acids, proved to be unnecessary, the sulphonic acids of tricyclic compounds exhibiting sufficient tanning action even without condensation. However, this process led to some improvement in the properties of the tanning agent, more rapid dyeing of the leather, and considerable lightening. The optimum effect was achieved with a small quantity of formaldehyde, 0.1–0.2 mole per mole of anthracene (compared with 0.5 mole of aldehyde per mole of phenol or naphthalene). In order to diminish the acidity the product was partly neutralised with sodium carbonate. In its final form it was a mixture of sulphonic acids, their sodium salts, and sodium sulphate.

The above process was put into practice at the Rubezhanskii Chemical Works with the production of two brands of tanning agents, AN (anthracene normal) and AK (anthracene condensed)†. They were widely used in the leather industry, especially the AN brand, which found application up to the end of the 1950s in the manufacture of sole leather.

In order to improve the colour of leather obtained by tanning with anthracene syntans, the sulphonated mass was oxidised with sodium hypochlorite, chlorine, and dichromate. Oxidation produced considerable clarification of the tanning solutions, but had little effect on the colour of the leather. However, provided that the sulphonated mass had first been condensed with formaldehyde, oxidation gave a very favourable effect [12]. Production of the tanning agent AKO (anthracene condensed, oxidised) involved the operations of sulphonation of crude anthracene, condensation with a small quantity of formaldehyde, neutralisation, crystallisation of sodium sulphate, making alkaline with caustic soda, oxidation with chlorine, and acidification with sulphuric acid. This tanning agent conferred a light, natural colour on the leather, but the complexity of the technique prevented its introduction into industry.

Oxidation with dichromate provided a considerably simpler method of obtaining the tanning agent. After condensation with formaldehyde the sulphonated mass was treated with a small quantity of water to lower the viscosity, and was three-quarters neutralised with sodium carbonate. The product was then oxidised with a concentrated solution of sodium dichromate, in amount such that all the remaining acid was neutralised by the bases formed on reduction of the dichromate [13]. The dry tanning agent comprised 30% of chromium sulphonate, 40% of sodium sulphonate, and 30% of sodium sulphate [14].

The tanning action of this syntan (Bestan AS) was considerably greater than that of the anthracene brands, since it was accomplished not only by the anion of the sulphonic acid but also by the chromic cation. The leather obtained was well formed and was stable to temperature. But the most valuable aspect was the safety in use of Bestan AS. In contrast to the anthracene brands, this tanning agent contained no free sulphonic acids. The acidity of its solutions was due solely to hydrolysis of the chromium salts. This kept the active acidity at a relatively low level, and conferred a buffer stability on the solutions, thereby preventing the possibility of hydrolysis of the collagen with weakening of the fibre [14].

Manufacture of Bestan was begun by the Rubezhanskii Chemical Works in 1930, and production soon reached several thousand tons per annum.

In 1934 the building was completed at Konstantinovka (Donets Region) of a factory for the manufacture of synthetic tanning agents. This works' range included five brands of syntans and an auxiliary type–Bestan AS, Bestan N (from naphthalene), the anthracenic AN and AK, and the naphthalenic NK–among which AK and Bestan AS were used for the accelerated tanning of Russia leather by a syntan–vegetable process, in which a considerable proportion of vegetable tannins had been replaced by synthetic tanning agents. The practical value of the brands AN and NK was determined mainly by their dispersing action on vegetable tannins. Their application to the manufacture of sole leather considerably improved the solubility of the vegetable extracts, stabilised the solutions [15], and accelerated the tanning process. Syntan NK has been widely used for this purpose up to the present time.

B. Auxiliary Syntans for Special Purposes

Other conditions for synthetic tanning agents arose in the West during the period following the First World War. As has already been stated, their use in Germany as substitutes for vegetable extracta almost completely ceased. However, specific features of these products maintained interest in their use for special purposes in the manufacture of both vegetable-tanned and chrome-tanned leather. As a consequence of this, new processes continued to be developed in the West for obtaining synthetic tanning agents. These processes were essentially variations on known methods. They can be divided into several groups: (*a*) the range of starting materials was expanded to naphthalene homologues, tetralin, benzylnaphthalene, naphthols, aromatic hydroxy-carboxylic acids, ethers of phenol with aliphatic alcohols, and esters thereof with aliphatic acids; (*b*) substituents–chloro-, nitro-, and amino-groups–were introduced into the aromatic rings; (*c*) various substances–acetaldehyde, paraldehyde, acetone, carbohydrates, sulphur, sulphur monochloride–were condensed with naphthalene- and hydroxybenzene-sulphonic acids; and (*d*) the sequence or the conditions of the operations–condensation under pressure, condensation at the instant of formation of the aldehyde (by passing acetylene into the sulphonated mass in the presence of a mercury salt), condensation of aromatic compounds by means of an aldo-group or an alcoholic group present in them, condensation before sulphonation, the introduction of substituents before or after sulphonation, the sulphonation of a compound containing an aldo-group or an alcoholic group and subsequent condensation with an unsulphonated compound–were varied.

These and similar modifications, described in European and American patents, are summarised in Bergmann and Grassmann's encyclopaedia of the leather industry [16]. It must be said that only a few of them were used industrially.

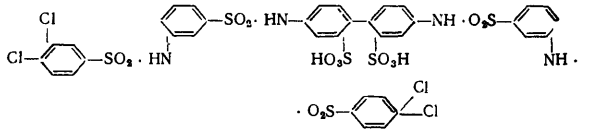
By contrast, in the manufacture of special-purpose auxiliary syntans based on hydroxybenzene- and naphthalene-sulphonic acids, various secondary procedures came into wide practical use, with the aim of improving the properties of the tanning agent, intensifying some particular

† The name "anthracene" is, of course, conventional indicating that the product has been obtained from crude anthracene.

feature in relation to a definite purpose, or increasing convenience in use. Among such procedures are removal of the inorganic portion, control of acidity, neutralisation with volatile bases (ashfree state), the addition of various salts (sodium chloride, sodium hydrogen sulphate, or potassium oxalato-aluminate, or -chromate, or -titanate) addition of organic acids (acetic, formic, oxalic, lactic), addition of preparations to prevent discoloration by iron ions (Trilon B)[17]. The differences between many brands of auxiliary syntans, even those manufactured at the present time, reduce to the use of particular supplementary procedures of the above type.

Special difficulties were presented by the synthesis of tanning agents which would make it possible to obtain a pure white leather fast to light, in particular a leather which would preserve its natural grain and colour (e.g. the leather of reptiles).

A great advance on these lines was represented by tanning agents proposed at the beginning of the 1930s, which contained several aromatic rings linked by sulphonamide groups[18]. It was found that the $-SO_2.NH-$ group, like a hydroxy-group in an aromatic ring, was a "tannophore", and a compound containing three or four such groups in the molecule possessed active tanning power. An industrial tanning agent of this type, manufactured in Germany by the firm IG. Farbenindustrie AG. under the brand name Tannigan LL, was identified and reproduced[19]. It was prepared from benzidine-2,2'-disulphonic acid by acylation with *m*-nitrobenzenesulphonyl chloride, followed by reduction of the nitro-group and further acylation with dichlorobenzenesulphonyl chloride, which yielded:



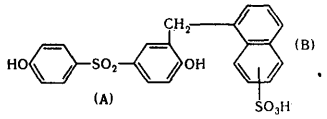
This syntan gave a white leather highly resistant to light, and also possessed considerably greater forming power than any other auxiliary tanning agent known at that time. It was also of theoretical interest, since it was the first individual, crystalline tanning agent. Brands of tanning agents of polysulphonamide type are still being manufactured in the Federal Republic of Germany.

Colourless syntans, stable to light and based on phenol, were also proposed, A peculiarity in their method of preparation was that the intercyclic methylene link formed by condensation with formaldehyde was replaced by other groups, such as $C(CH_3)_2$, $CH_2.NH.CO.NH.CH_2$, and SO_2. This resulted in a considerable diminution in the oxidisability of the condensation product compared with diphenylmethanediol, and on storage the leather preserved a light colour for a long time.

An isopropylidene link is formed by condensing the hydroxybenzenesulphonic acids with acetone[20], and a ureylenedimethylene link by simultaneous condensation with formaldehyde and urea[21] or by condensation with bishydroxymethylurea[22]. The use of urea to lighten leather was widely introduced into practice, and at the present time is often employed in the synthesis of tanning agents belonging to various chemical types.

Among the above variants, however, the use of aromatic hydroxy-compounds in which the rings were linked through a sulphonyl group acquired the greatest value, primarily bis-*p*-hydroxyphenol sulphone, which became one of the most important intermediates in the synthesis of tanning agents. Syntans based on bishydroxyphenyl sulphone are prepared in three ways–(*a*) sulphonation followed by condensation with an aldehyde[23], (*b*) simultaneous condensation with an aromatic sulphonic acid and formaldehyde[24], and (*c*) sulphomethylation and condensation with formaldehyde[25]–brands for white leather being produced mainly by the latter two methods.

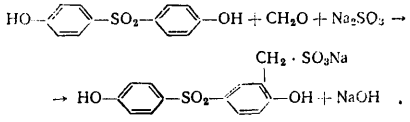
The purpose of simultaneous condensation of the sulphone with naphthalenesulphonic acid is to link the two molecules through a methylene group, with formation of a water-soluble product:



A and B condense in the various permutations so that the final product is a mixture of $A.CH_2.A$, $B.CH_2.B$, and $A.CH_2.B$, together with a certain amount of unchanged A and B. Reich[26], in an investigation of the analogous product of the simultaneous condensation of bis-*p*-hydroxyphenyl sulphone and 6-hydroxynaphthalene-2-sulphonic acid with formaldehyde, showed that only 50% of the sulphone gives a mixed condensation product, the remainder going into colloidal solution as a consequence of the protective action of the sulphonic acid.

Tanning agents of this type, obtained from pure starting materials (sulphone and naphthalene), yield a white leather having a plastic surface layer. The conditions for carrying out the synthesis were studied, and the dependence of the tanning action–the increase in the forming and filling power–on the relative proportions of sulphone and naphthalenesulphonic acid was established[27].

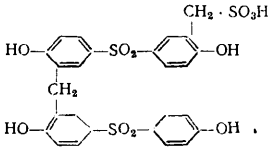
The method of sulphomethylating (or ω-sulphonating) a sulphone consists in the simultaneous condensation of the sulphone with formaldehyde and with sodium sulphite or a mixture of the sulphite and the hydrogen sulphite. This involves the introduction of a sulphomethyl group into the ring:



In the presence of excess of the aldehyde, ω-sulphonation is accompanied by condensation of the sulphone with the aldehyde[28].

As in the co-condensation of bishydroxyphenyl sulphones with naphthalenesulphonic acid and formaldehyde, sulphomethylation yields products which surpass the average of auxiliary syntans in their tanning action. The solubility of a product and its tanning action are greatly dependent on the relative proportions of sulphone, sulphite, and formaldehyde.

A detailed investigation of the condensation of bis-*p*-hydroxyphenyl sdulphone with formaldehyde[29] led to the isolation in crystalline form of an intermediate hydroxymethyl derivative, and it was shown that, with molar proportions of sulphone, sodium sulphite, and formaldehyde of 1.10 : 1.0 : 0.5, the chief product is a tetracyclic compound containing one sulphomethyl group[30]:



The advisability was also established[31] of conducting the process in two stages: (*a*) the sulphone was condensed with formaldehyde in the presence of small amounts of the sulphite as catalyst; and (*b*) sulphomethylation was effected with formaldehyde and the sulphite present in equimolecular quantities. This process was used for several [years?] to produce in an experimental plant Tanning Agent SB (Sulphone White), which was used by the works as a levelling agent in the dyeing of chrome leather in pale colours.

III. SYNTANS USED AS SUBSTITUTES FOR VEGETABLE TANNINS

A. Development of Methods for the Production of Substitute Syntans in the USSR

During the middle 1930s synthetic tanning agents of a novel type appeared in Germany under the name "Tannigans extra". Leather obtained by tanning with these syntans was closely similar to vegetable-tanned leather in physical properties and in yield by volume and weight. This permitted them to be used as complete substitutes for natural tanning materials.

The patent literature of those years revealed no fundamentally new methods for the synthesis of tanning agents, and the mode of production of Tannigans extra remained unknown, although papers in the periodical literature indicated that the new syntans were distinguished from the previous (auxiliary) syntans in starting materials, the functional groups responsible for their tanning action, and the active acidity of the solutions[32].

From this it must be supposed that the German Tannigans extra were weak acids: i.e. unlike the auxiliary syntans they could not be classed as aromatic sulphonic acids. This formed the starting point for the work of Konovalenko et al. on the preparation of a tanning agent free from sulpho-groups condensing resorcinol with acetaldehyde[33]. Their product, to which the name "Rezotan" was given, possessed good tanning power, but its industrial production was prevented by its high cost.

At the same time an investigation was being made at the Ukrainian Institute of Applied Chemistry into the possibility of obtaining substitute syntans of the sulphonic-acid type by varying the conditions under which the individual stages were conducted and varying the quantitative proportions of the reactants[34]. This work was based on an observation made in an attempt to increase the organic content in the anthracene brands by introducing a phenolic, Novolak resin into the sulphonated mass. It was supposed that excess of sulphuric acid present in the sulphonated mass, although at a low concentration, would be able to sulphonate a certain amount of the resin, with a consequent diminution in the organic content of the tanning agent, and an increase in the so called quality–the content of adsorbable material.

It was found that the resin was sulphonated to a very slight extent, but a homogeneous product, forming quite stable colloidal solutions, was obtained by stirring it with the sulphonated mass and heating[36]. By means of such dispersion it proved possible to bring into a soluble state up to 100% of resin based on the quantity of crude anthracene in the sulphonated mass. With increase in the quantity of resin the stability of the colloidal solution diminished: the quantity of resins which could be salted out by electrolytes increased. This was accompanied by increase in the volume yield and the tanning coefficient of the leather [(Table 1)]: i.e. its properties approached closer and closer to those of vegetable-tanned leather.

A similar result was obtained with naphthalenesulphonic acids condensed with formaldehyde. Thus recourse to other chemical types was not necessary in order to obtain heavy-duty synthetic tanning agents, possessing fundamentally new technical properties towards leather, for this could be accomplished within the limits of the same type of aromatic sulphonic acids as for the production of light duty, auxiliary syntans. It was achieved by increasing the organic loading on the sulpho-group by intermolecular bonding of a sulphonic acid with a phenolic resin of low degree of polymerisation.

Table 1.

Phenolic resin, % on crude anthracene	Vol. yield of leather, % on hide	Tanning coeff. of leather
0	165	20
30	222	25
50	251	31
100	292	55

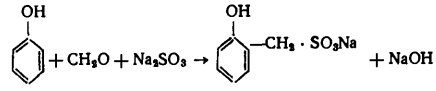
The dispersion of a phenolic resin in the sulphonic acids raised their tanning action to a higher level: i.e. it "improved" the tanning agent, as it were. Hence our brand letters–AO and NO–for the new anthracene and naphthalene tanning agents.

A very favourable result was obtained by dispersing a phenolic resin in ligninsulphonic acids (concentrates of waste sulphite liquors from the manufacture of cellulose)[34]. These liquors were suggested for use in leather production as early as the end of the nineteenth century, and were employed in industry, after preliminary purification, under the name of sulphite–cellulose extracts. However, their very feebly developed shaping power allowed them to be used only as an ancillary product, predominantly as a filler to increase the density of the leather and raise the yield by weight. Numerous attempts to improve the tanning power of sulphite–cellulose extracts produced only a very insignificant effect[37].

The dispersion of a phenolic resin in sulphite concentrates led, as with aromatic sulphonic acids, to a series of syntans the later members of which were not inferior to vegetable tannins in their tanning ability. These improved sulphite–cellulose extracts were denoted by the letters LF (lignin–phenolic).

The results of applying the same method to condensed hydroxybenzenesulphonic acids were very significant for subsequent work. Dispersion of a phenolic, Novolak resin in them yielded purely phenolic syntans, which exhibited a gradual change in tanning ability from the auxiliary type to well defined full substitutes[38]. This suggested the possibility of obtaining a similar series of phenolic syntans not by dispersing but by directly sulphonating the phenolic resin with a diminished quantity of sulphuric acid, so that only a proportion of the phenolic resins could undergo sulphonation, the proportion decreasing as the molar ratio of sulphuric acid to phenol was decreased. The part of the resin which had not been sulphonated would then be dispersed in the sulphonated product. This hypothesis was confirmed. Soluble products could be obtained even with a molar ratio of monohydrate to phenol in the resin of 0.15 : 1.00.[39] The corresponding series of tanning agents proved to have the widest range of variation in technical properties towards leather. The series was denoted by FT (phenolic heavy)[35].

Decreasing the ratio of sulphonating agent to the phenol, which was used to obtain the FT series of syntans, was applied also to another method of obtaining synthetic tanning agents–the condensation of phenols with formaldehyde and sodium sulphite, resulting in sulphomethylation of the phenol (termed also ω-sulphonation).



This process, known since the early years of the appearance of industrial syntans [40,41], acquired no practical value, since it yielded tanning agents of the same light type as did the condensation of hydroxybenzenesulphonic acids with formaldehyde. When the quantity of sulphite was diminished and that of the aldehyde increased, products were obtained which were typical heavy syntans, denoted by the letters FB (phenolic with a sulpho-group in the side-chain).

Thus by the prewar period synthetic methods had been developed which yielded a number of Soviet brands of synthetic tanning agents, making it possible, depending on the type of leather production, to replace vegetable extracts either completely or to a considerable extent [35]. Since 1938 these new brands have been manufactured in experimental production batches, and have been tested with positive results on various types of leather. The potentially most useful were the purely phenolic tanning agents of the FT series and ligninsulphonic concentrates improved with a phenolic resin (LF series). By combining them it was possible to obtain, without the use of vegetable extracts, both stiff and supple types of leather (sole leather and Russia leather) having normal physicomechanical properties.

B. Processes employed in the Synthesis of Soviet Heavy-duty Syntans

1. PREPARATION OF PHENOLIC RESIN

In Stiasny's original patent two methods were proposed for obtaining condensation products of hydroxybenzenesulphonic acids with formaldehyde, which differed in the sequence in which the operations of sulphonation and condensation were carried out. No distinction was made between them in the patent, and the first tanning agent, Neradol D, was obtained by sulphonating phenol and then condensing with formaldehyde. Subsequently Wolesensky [42] noted peculiarities in the products obtained by these methods, and pointed out that the second method (preliminary condensation of phenol with the aldehyde) yields a well filled leather, but involves difficulties in sulphonation and the possibility of "charring" of the resin.

A comparative study of the two alternatives has confirmed the difference in properties of the leather pointed out by Wolesensky, but no difficulty was found in the sulphonation. On the contrary, prelimary condensation had a decided advantage over subsequent condensation also in conducting the synthesis. With the stoichiometric proportion of sulphuric acid stable solubility for the resin was reached considerably more rapidly and at a less elevated temperature. With smaller amounts of acid a soluble condensation product could not be obtained at all from the sulphonated phenolic mass. In the synthesis of heavy-duty phenolic tanning agents, therefore, preliminary condensation of the phenol with aldehyde is of very great value.

The condensation of phenols with formaldehyde has been studied thoroughly, and its mechanism is known. The preparation of synthetic tanning agents requires a resin of Novolak type: i.e. condensation should be conducted in acid medium. A resin obtained by alkaline condensation leads to complications in subsequent sulphonation, owing to the presence of hydroxymethyl groups and the consequent tendency to thermosetting. In the presence of concentrated sulphuric acid and at high temperatures such a resin readily forms compounds which do not pass into a soluble state, diminish the yield of tannins, and lower the quality of the product.

The relative proportions of aldehyde and phenol effect the quantity of free phenol in the resin and the mean molecular weight of the oligomer. Subsequent sulphonation imposes no special restrictions on the degree of condensation. Up to 0.8 mole of aldehyde per mole of phenol, stable solubility of the product is reached even with small amounts of sulphuric acid. With regard to the relation between the extent of condensation and tanning ability, it was found that, contrary to expectation, no appreciable change in tanning properties was observed from the stoichiometric proportion and above. The optimum ratio can be regarded as 0.6 mole of aldehyde per mole of phenol. The condensation product is a mixture of molecules containing different numbers of rings linked through methylene groups. Analysis indicates that, with the above reactant ratio, the free phenol content is 15%, while the mean molecular weight of the polymer is about 500.

2. SULPHONATION OF PHENOLIC RESIN

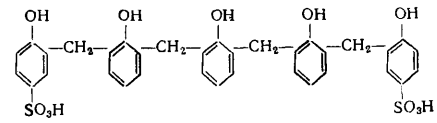
Sulphonation is the stage in the synthesis which determines the principal tanning parameters of the product. The same phenolic resin can yield tanning agents differing in forming and filling power from the lightest to complete substitutes, merely by variation in the proportion of acid to the resin. As this ratio is decreased, it becomes more difficult to obtain a product having stable solubility: it is necessary first to lower the moisture content of the resin, increase the acid concentration, raise the temperature, and prolong the process.

After separation from water the phenolic resin contains 15–20% of moisture. It is easily sulphonated by concentrated sulphuric acid in close to stoichiometric proportions (1.0 mole of monohydrate per mole of phenol), as is required in the preparation of light syntans. For heavy syntans the amount of acid should be halved, and here it is necessary to lower the moisture content in the resin to 3–4%. With further decrease in the proportion of acid, dissolution is achieved only by using oleum.

The results obtained on the relation between the tanning action of the product and the ratio of the reactants in sulphonation of the resin are given in Table 2.[35]

When small amounts of acid are used for sulphonation, a large proportion of it undergoes reaction. Thus with 0.5 mole of acid on the phenol, not more than 10% of the acid taken remains free in the sulphonated mass [43]. Calculation indicates that in this case the equivalent weight of the sulphonic acid is ~300.

With the molecular weight indicated above for a polymer of a normal phenolic resin ($M = 500$), the molecule of the tanning agent comprises on the average five phenolic rings associated with two or three sulpho-groups:



3. SECONDARY CONDENSATION

A feature of the entire series of tanning agents obtained by sulphonating a phenolic resin is their slow penetration into the leather in comparison with tanning agents obtained by the first alternative, i.e. products formed by the condensation of hydroxybenzenesulphonic acids. However, with the first few members of the series having a high proportion of sulphuric acid to resin this retardation is slight. As the quantity of acid decreases, the tendency of the tanning agent solutions to coagulate increases, and penetration into the leather becomes increasingly difficult, entailing very serious difficulties in practical application.

Table 2.

Molar ratio of acid (monohydrate) to phenol	Quality (ratio of adsorbable to dry substance)	Vol. yield of leather	Tanning coeff. of leather
0.9	49.5	220	34
0.5	65.9	301	56
0.4	79.0	322	60
0.3	84.6	378	87

This defect could be overcome by introducing an additional condensation of the sulphonated mass with small amounts of formaldehyde [44], which was carried out, after preliminary dilution of the sulphonated mass with water, at a low temperature (not above 50°C). Raising the temperature results in the appearance of insolubles, or even in complete insolubility of the product. A second condensation enhances the stability of the solutions, increases the content of tanning agents, considerably accelerates penetration into the leather, and improves its colour because dark, resinified particles are not now retained on the surface, but penetrate inside the leather. Thus a secondary condensation provides a very important method for all modifications of the given series of tanning agents, while for the heavier agents (in practice the most valuable) this can be regarded as essential.

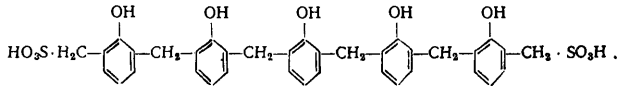
The course of the process depends to a considerable extent on the reaction of the medium. A decrease in acidity (partial or complete neutralisation of the sulphonated mass) lowers the reaction velocity, and condensation can be effected without complication at temperatures up to 75°C.[45] The quantity of aldehyde introduced in the second condensation has a fundamental effect on the properties of the tanning agent. It was established that, as the quantity of formaldehyde increased, the tanning properties passed through an optimum, after which they deteriorated considerably. With a normal resin (see above) this optimum occurs at a molar ratio of formaldehyde to phenol of ~0.1 : 1.0.

The presence of a maximum on the curve for the variation in the tanning properties of phenolic syntans as the quantity of formaldehyde is increased applies only to condensation after sulphonation. Such a maximum is not observed with preliminary condensation. Consequently this finding cannot be attributed to the increase in size of the molecule. It must probably be ascribed to the introduction of hydroxymethyl groups into the phenolic rings, which takes place under the mild conditions of the secondary condensation. In small quantities hydroxymethyl groups may have a favourable effect, by enhancing the hydrophilic character of the product and promoting the penetration of enlarged particles of the tanning agent into the fibrillar structure of the leather. However, the intensification of this property leads to a diminution in bonding and affects the occurrence of osmotic processes linked with the formation of the structure of leather.

4. SULPHOMETHYLATION OF PHENOL

With formaldehyde and sodium sulphite phenol undergoes two simultaneous reactions—the usual condensation with an aldehyde and sulphomethylation or introduction of a $CH_2.SO_3H$ group into the phenolic ring—the degree of condensation and the extent of sulphomethylation (mean equivalent weight of the sulphonic acid) depending on the proportions of the reactants and also on the process conditions. The best results with respect to product quality and reproducibility are obtained when the process is conducted in stages. The first stage—preliminary condensation of phenol with formaldehyde—is conducted under the same conditions—in acid medium with 0.5—0.6 mole of aldehyde based on the phenol—as for the sulphonic acid type of tanning agent. The second stage (sulphomethylation) requires, according to the equation for the reaction, equimolecular quantities of formaldehyde and sulphite; thus the proportion of sulphite based on the phenolic resin predetermines the proportion of formaldehyde. The sulphite : phenol ratio, however, can be varied within wide limits. Depending on this the tanning properties of this type of syntans also vary, just as those of the condensed hydroxybenzenesulphonic acids vary with the acid : phenol ratio adopted in sulphonating the resin.

By decreasing the proportion of sulphite to the initial phenol in the resin it is possible to obtain a series of tanning agents (FB) having enhanced tanning power like the FT series, obtained by sulphonating a phenolic resin. The molecule of the FB tanning agent from a normal resin with a molar ratio of sulphite to phenol of 0.5 : 1.0 contains on the average two sulphomethyl groups associated with five phenolic rings:



This product is a complete substitute syntan.

During sulphomethylation part of the aldehyde is consumed in further condensation with the phenolic resin, so that the sulphite does not enter completely into the condensation. With small amounts of sulphite this may result in inadequate solubility of the product, to prevent which it is advisable to increase the proportion of formaldehyde, i.e. to add rather more than an equimolecular quantity relative to the sulphite. Use of an increased proportion of aldehyde gives a soluble product even with 0.25 mole of sodium sulphite based on the initial phenol. As with an additional concentration after sulphonation of the resin, the variation in tanning properties with increasing amount of formaldehyde passes through an optimum here.

Compared with the analogous tanning agents of the FT series, the FB syntans, obtained by sulphomethylation of a phenolic resin, are distinguished by improved filling power and are less sensitive to changes in the active acidity of the solutions [35].

5. DISPERSION OF PHENOLIC RESIN IN SULPHONIC ACIDS

A phenolic resin is brought into colloidal solution by prolonged stirring with a solution of a sulphonic acid at

80–100°C. The process is favoured by high solute concentrations. Dilution considerably lengthens the process and diminishes the amount of resin which can be dispersed.

Before addition of the phenolic resin the sulphonic acids should be brought to their normal tanning power by condensation with aldehyde. Dispersion of the resin in uncondensed naphthalene- or hydroxybenzene-sulphonic acid gives a tanning agent of poor quality, which cannot be substantially improved by subsequent condensation of the dispersed product with formaldehyde.

Sulphonic acids exhibit active dispersing power only in the free state. Salts of sulphonic acids do not possess this ability, even in concentrated solutions, but sulphonic acids which have undergone normal improvement with a phenolic resin can, in the concentrated state or in solutions, be neutralised or subjected to other chemical treatments without breakdown of the colloidal system.

As has already been stated, the quantity of resin which can be introduced into the sulphonic acid depends on the solute concentration. Therefore the preliminary condensation of sulphonic acids with a considerable volume of formalin is an unfavourable factor in this respect. Modified processes in which preliminary condensation is not required, or is limited to a small quantity of aldehyde, permit greater improvement (e.g. the sulphonic acids from crude anthracene). The dispersing power depends also on the nature of the acid. In this respect sulphonic acids of tricyclic hydrocarbons are superior to those of bicyclic hydrocarbons. But ligninsulphonic acids (sulphite liquors) are especially active dispersing agents for phenolic resins: even in the neutralised state at a concentration not exceeding 50% they can bring up to 30% of the resin (based on the dry substance) into colloidal solution.

The tanning properties of the products obtained by dispersing a phenolic resin in any sulphonic acid are improved by further condensation with small amounts of formaldehyde.

6. ADJUSTMENT TO NORMAL ACIDITY

The final stage is adjustment of the acidity of the tanning agent to that required for practical application. Products of sulphonation of the resin or its dispersion in aromatic sulphonic acids require to be neutralised, which is accomplished with sodium carbonate or ammonia to a slightly acid reaction. Sulphomethylation produces a considerable quantity of alkali, and the product must be acidified with sulphuric acid. Dispersion of a phenolic resin in concentrates of sulphite liquors takes place in weakly acid medium, and these tanning agents do not require adjustment.

The shortage of phenol during the postwar period made it necessary to use more readily available starting materials—technical mixtures of phenols which could be extracted from tar waters formed in the thermal processing of bituminous shales and in the low-temperature carbonisation of coal. Work on these lines was conducted in the Central Scientific Research Institute for the Leather Industry by Konovalenko, Khadyk, Kuraitis, Golubeva, and Filippova.

By means of procedures developed previously (condensation with formaldehyde and subsequent sulphomethylation or dispersion in sulphonic acids) it proved possible to obtain from the extractable phenols a series of brands of substitute syntans, which found wide practical application under the designations No. 5, No. 12, SL, and SPS [46-48].

The most interesting of these tanning agents is SPS, obtained by the method proposed by Konovalenko [49]. The extractable shale phenols (mainly homologues of resorcinol) are condensed by this method with ligninsulphonic acids and formaldehyde, and the condensation product is dispersed in the spent liquor from the fermentation of sulphite-cellulose liquors to alcohol. From its tanning power SPS cannot be regarded as a full substitute, but it confers a light natural colour on leather and is readily compatible with other types of tanning agents.

Syntans obtained by the sulphomethylation of a polyphenolic resin possess substantial disadvantages—the dark colour and unpleasant odour which they confer on the leather, and also the inadequate standardisation of the product due to the variability in composition of the raw material—which suggests that such brands will not be kept in the range, and in the very near future will be replaced by syntans based on crystalline phenol. The production of brands from pure phenol by the methods described above has been growing rapidly during recent years. Among them are No. 2 [50] (an analogue of ST-50, differing from the latter in the use of ammonia for neutralisation), No. 3 (identical with LF), and FB-2 [51] (a modified form of FB, in which phenol has been replaced by the phenolic fraction of coal-tar).

C. Methods of Producing Substitute Syntans Abroad

At the end of the war information was published on German materials [52] and also literature surveys [17] on the production of German brands of synthetic tanning agents, so that it became possible to compare the development of ideas and practical methods for obtaining substitute syntans in the USSR and in Germany.

It turned out that the features which were mentioned in the pre-war foreign literature (see above) were secondary criteria. The German Tannigans extra did not belong to any new chemical types, but were the same sulphonic acids improved with phenols or their derivatives. Thus the general direction of German and Soviet work in producing substitute syntans was the same, but the initial attitudes and the methods by which improvement was accomplished were fundamentally different. The same task—to enlarge the particle size and increase the phenolic loading on the sulpho-group—was understood differently by the German chemists and by ourselves. Soviet investigators started from the observed possibility of dispersing the phenolic resin, and saw a solution to the problem in obtaining a coarse colloidal particle by intermolecular interaction between the phenolic oligomer and condensed sulphonic acids. German chemists thought it necessary to increase the size of the tanning agent molecule, i.e. to combine phenolic and sulphonic-acid components chemically by condensing them simultaneously with aldehydes ("mixed" condensation) [53].

In spite of the fundamental difference, these methods yield products which are analogous chemically and exhibit similar behaviour towards leather. As a consequence of this there is a considerable affinity between the German Tannigans extra and the same types of Soviet brands of heavy syntans.

It should be remarked that mixed condensation is a more complicated procedure than dispersion. It breaks down into several individual condensation of the initial compounds in various combinations, and results in the formation of a mixture of substances differing in chemical composition and structure, whereas with dispersion the final

result is determined unambiguously by the relative proportions of the components. In virtue of this, colloidal improvement creates more favourable conditions for studying theoretical aspects of the interrelation between the structure and the tanning properties of synthetic tanning agents. This may well be the reason why the researches aimed at producing the Soviet substitute syntans led to broader generalisations than did the foreign work. Among such generalisations are—(*a*) the absence of a direct connection between the chemical class of a tanning agent and its properties in relation to leather, (*b*) the concept of the chemical type of tanning agent as a kind of "homologous series" with a gradual change in tanning power, (*c*) the difference in the ratio between the parameters of forming and filling power for different chemical types ("homologous series" of tanning agents), and (*d*) the possibility of a rational specification of syntans from the point of view of leather technology, based on the ratio of the parameters representing forming and filling power[54].

Examination of prewar German methods for obtaining substitute syntans and their comparison with postwar methods described in foreign patents show that the principles laid down in this field in the 1930s have been fully maintained. A few new specialised brands of synthetic tanning agents have appeared since the war, but nothing fundamentally novel has been introduced into the methods of synthesising the substitutes. The present-day range of substitute syntans abroad comprises brands belonging to the same chemical types as were developed in Germany and in the USSR during the prewar period.

1. IMPROVED SULPHONIC ACIDS OF AROMATIC HYDROCARBONS

Tanning agents of this type are obtained by linking aromatic sulphonic acids with phenolic rings through a methylene group. This can be accomplished by the simultaneous condensation of sulphonic acids and phenols with formaldehyde, or by the condensation of sulphonic aicds with phenolic alcohols or resol resins[55]. Methods have been described also for linking through sulphur (condensation with sulphur monochloride) or through the sulphonyl group heating naphthalenesulphonic acids with hydroxybenzenesulphonic acids to a high temperature, when sulphonic acids of mixed hydroxyphenyl naphthyl sulphones are formed)[56]. Naphthalene- or benzylnaphthalene-sulphonic acid is used as the acid component, and ordinary phenol, tricresol, a polyhydric phenol, or bishydroxyphenyl sulphone as the phenolic component.

The simultaneous condensation of hydrocarbons with phenols is made difficult by the marked difference in their reactivity towards formaldehyde. As a consequence, the condensation products are very inhomogenous in composition, and contain a considerable quantity of insoluble compounds dispersed in the sulphonic acids.

Tanning agents of this type are not above the average in forming and filling power, and they cannot be regarded as complete substitutes. Rather they must be included in an intermediate group of syntans, destined for the manufacture of light types of leather or for combination with vegetable extracts in relatively small proportions.

The best product of this type is that resulting from the mixed condensation of naphthalenesulphonic acids with bishydroxyphenyl sulphone. With a high sulphone : naphthalene ratio it reaches the level of complete substitutes in its tanning action[27].

2. IMPROVED HYDROXYBENZENESULPHONIC ACIDS

This is the most widely represented type of tanning agents, and several methods have been proposed for obtaining them—mixed condensation of hydroxybenzenesulphonic acids with phenols and aldehyde, condensation of hydroxybenzenesulphonic acids with phenolic alcohols, etc.

Phenol, tricresol, the naphthols, mono-, and dihydroxybiphenyls, polyhydric phenols, and bishydroxyphenyl and bishydroxytolyl sulphones have been used as the initial compounds containing phenolic hydroxyls. Besides the usual mixing of the components, mixtures of them are sometimes obtained from the same starting material by an incomplete intermediate process. For example, a mixture of hydroxybenzenesulphonic acid and bishydroxyphenyl sulphone is obtained from phenol by heating it to a high temperature with a quantity of sulphuric acid insufficient for sulphonation[57]. The preliminary or mixed condensation of hydroxybenzenesulphonic acids with formaldehyde and phenols is often carried out with the addition of urea, which improves the colour of the leather[58].

The most valuable variant in practice is sulphonation of a Novolak phenolic resin until it is completely soluble, followed by condensation with formaldehyde[59]. The tanning agent "extra B" obtained in this way is very similar in tanning properties to our FT-50.[60]

Tanning agents of this type are characterised by a predominance of forming over filling ability. Their chief purpose, therefore, is the tanning of Russia leather, as well as of the less durable types of leather for the base of footwear and for technical uses.

3. PRODUCTS OF THE SULPHOMETHYLATION (ω-SULPHONATION) OF PHENOLS

Sulphomethylation is one of the processes generally used to obtain substitute syntans, and is employed in various ways. The starting materials used are phenol and its homologues, polyhydric phenols, dihydroxybiphenyl, bishydroxyphenyl sulphone, or products of their preliminary condensation with formaldehyde in acid or alkaline medium. In foreign practice, however, this process is probably used predominantly to obtain tanning agents of mixed types. By itself the ω-sulphonic-acid type is of secondary practical value. This can be explained by the lower solvent power of such sulphonic acids for vegetable extracts in comparison with the usual hydroxybenzenesulphonic acids.

Independent application is found mainly with products of the sulphomethylation of bishydroxyphenyl sulphones[61].

4. LIGNINSULPHONIC ACIDS IMPROVED WITH PHENOLS

A feature of substitute syntans obtained by improving ligninsulphonic acids is their good filling power and the enhanced durability conferred on the leather, which makes them especially valuable for the manufacture of sole leather. With respect to the place they occupy in the foreign range, tanning agents of this type are as important as improved hyroxybenzenesulphonic acids.

The starting material for their production consists of the waste lyes from the manufacture of sulphite cellulose or the spent liquor remaining after their fermentation into alcohol. These liquids are usually freed from calcium salts; sometimes they are subjected to other forms of preliminary treatment, e.g. heating with alkalis under pressure to diminish the quantity of combined sulphurous acid.

A general method of improvement is the mixed condensation of sulphite concentrates with phenols or their derivatives in acid or alkaline medium[62]. The chief brand of this type, which has remained in the German range for thirty years, is a product of condensation with bishydroxyphenyl sulphone ("extra A"), which is similar to our LF in tanning properties[60].

Various ways of using mixed condensation to improve ligninsulphonic acids are given in patents. Conducting the process in two stages is of practical value: (*a*) preliminary condensation of a phenol or a sulphone with formaldehyde is followed by mixed condensation of the product with the sulphite liquor; (*b*) mixed condensation of the liquor with a phenol or a sulphone yields a product which is separated from the solution, and dispersed in a fresh portion of liquor. Ligninsulphonic acids improved with phenols are easily salted-out from solution by electrolytes. This enables a tanning agent of this type to be obtained as a solid product having a high content of tanning agent[63].

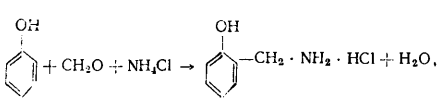
Together with tanning agents belonging to the individual chemical types described above, the foreign range contains a large number of brands of mixed types, i.e. obtained by combining two or more modes of improvement, or representing simply mixtures of ready made tanning agents of different types. For example, phenol (cresol) is condensed with a mixture of hydroxybenzene- and naphthalene-sulphonic acids[64]; phenol or bishydroxyphenol sulphone is condensed with a mixture of ligninsulphonic and aromatic sulphonic acids[65]; hydroxybenzene- or hydroxynaphthalene-sulphonic acids, after being condensed simultaneously with phenol and an aldehyde, are mixed with ligninsulphonic acids which have previously been improved by condensation with phenol and formaldehyde[66]; a product of the sulphomethylation of bishydroxyphenyl sulphone is subjected to mixed condensation with hydroxytoluenesulphonic acid, bishydroxyphenylpropane, and formaldehyde; etc.[67]

A noteworthy feature of the numerous variants of this kind encountered in patents of the war and postwar periods is that they reflect no tendency at all to further specialisation of the tanning agents in relation to leather technology, in particular any strengthening of the characteristics of substitute syntans. On the contrary, these modifications are directed to obtaining tanning agents of intermediate type as regards leather technology, in which the forming and filling ability is controlled at the level necessary for the solution of additional problems not directly connected with the replacement of vegetable extracts.

IV. NEW TYPES OF SYNTHETIC TANNING AGENTS

1. Amphoteric Tanning Agents

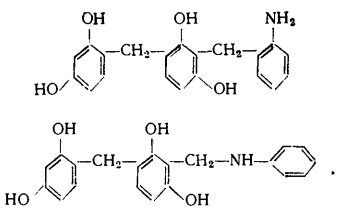
Up to the end of the 1940s all methods for obtaining synthetic tanning agents, whether operated industrially or only described in the literature, yielded products in which the tanning action was located in an anion. At the beginning of the past decade tanning agents of a new chemical type, have a tanning cation, appeared in the Federal Republic of Germany. Their mode of production, developed by Mauthe and Farber[68], consisted in the simultaneous condensation of an ammonium or an amine salt with a phenol and an aldehyde:



Compounds of this type dissolve readily in acid medium as substituted ammonium salts, and in alkaline medium as phenoxides. The tannophoric groups—phenolic hydroxyls—are located in the former case in the cation, and in the latter case in the anion. This gave rise to the name amphoteric synthetic tanning agents[69,70] which is really incorrect, since they exhibit tanning activity only in acid medium. In contrast to the usual synthetic tanning agents, the tanning power of amphoteric syntans (their combination with a protein) increases as the acidity diminishes. At the isoelectric point they are precipitated from solution. A characteristic property of the new tanning agents is the formation with anionic compounds—tanning agents, dyes, fat-liquoring sulphonated products—of insoluble salts: this property permits their use both as tanning agents and as fixing agents, anchoring the anionic products in the leather. This second use, which requires only a relatively small amount of the syntan, is of far greater practical interest than is the first. However, the simultaneous tanning action gives a substantial additional effect, which is a valuable distinguishing feature from other types of fixing agents.

The tanning action of amphoteric syntans depends on the nature of the initial compounds and on their relative proportions. In this respect these agents resemble anionic syntans. The tanning power of sulphonic acids improved with phenols increases with increase in the phenolic loading on the sulpho-group; in amphoteric tanning agents the phenolic loading on the amino-group has an analogous effect: as the amount of phenol combined with the amine increases, the tanning agent approaches closer and closer to the heavy type.

Products obtained by the Mannich reaction from phenols possess very weak tanning action, since they achieve stable solubility only at a high amine : phenol ratio. Products whose tanning action is comparable with that of substitutes can be obtained only by the simultaneous condensation of a polyhydric phenol with formaldehyde and an aromatic amine, e.g. by the condensation of resorcinol with formaldehyde and aniline with a molar amine : phenol ratio not exceeding 0.5 : 1.0. In this case the reaction can go in two ways, with formation of the compounds:



The condensation leads predominantly to a product of the type (I).

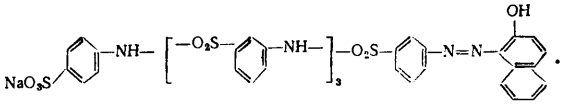
Methods were developed for obtaining amphoteric tanning agents based on technical mixtures of polyhydric phenols from tar water from the low-temperature carbonisation of coal. In the first modification the process is conducted in stages, the amine being introduced into the reaction in two portions with intermediate cooling[71]. This makes solubility easier to achieve, and enables mixtures of polyhydric and monohydric phenols to be used. In a second modification formaldehyde is replaced by bishydroxymethylurea[72], which lowers the heat of reaction and facilitates its occurrence.

When tried on an industrial scale the amphoteric tanning agent LAF, which we have obtained, exhibited a high tanning power.

2. Dyes with Tanning Ability

Acid and direct dyes exhibit some structural similarity to synthetic tanning agents. This explains their tanning ability, which is developed to different extents depending on the molecular weight and structural features[73]. In the usual dyeing of leather, in spite of the small consumption of dye, the tanning action of certain dyes has an appreciable effect on the physical properties of the surface layer. In comparison with syntans, of course, the tanning power of dyes is small, not surpassing the lower grades of the auxiliary type. However, it could be considerably strengthened by increasing the organic loading on the sulpho-group and introducing tannophoric groups into the molecule, provided that the chromophoric system is not disturbed.

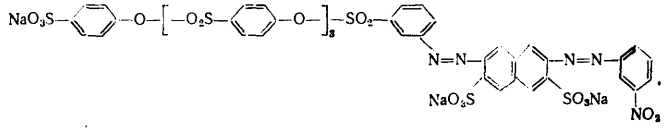
Dyes of this type were first prepared by Berkman and Gordinskii[74]. They were azo-dyes in which the diazo-component contained a polycyclic polysulphonamide chain as is usual for synthetic tanning agents of the polysulphonamide type[75,76]:



Further studies have been made of the synthesis and properties of polysulphonamide azo-dyes[77,78]. Analogous compounds were obtained containing sulphonamide groups in the coupling component, and symmetrical and unsymmetrical *cis*- and polyazo-dyes containing chromophores isolated by a polycyclic polysulphonamide chain.

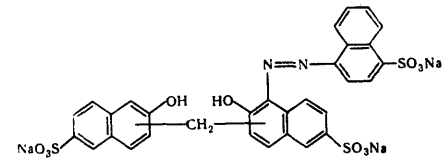
All these dyes exhibited high tanning power, evenness of coloration, and fastness to wet rubbing. The increase in levelling power is interesting, for this usually becomes worse with increase in size of the dye molecule. In the present case the colour is probably influenced favourably by the simultaneous differentiation of the fibre structure of the outer layer of the leather, which contributes to a uniform distribution of the dye.

Azo-dyes having similar properties are obtained[79] by introducing a polyaryloxysulphonyl chain or a mixed chain containing sulphonic ester and sulphonamide groups into the molecule[80,81]:



Polysulphonamide and poly(sulphonic ester) dyes are individual compounds, and can be obtained as crystals. By varying the length of the chain it is possible to obtain for each dye a series of compounds containing the same chromophoric system but differing in number of tannophoric groups and in molecular weight. This makes it possible to study certain aspects of the relation between the molecular structure and the physicochemical and dyeing properties of dyes[75,77,78,81].

Dyes which already contain tannophoric groups (phenolic hydroxyls), but exhibit only slight tanning activity, can be made active tanning agents by enlarging the molecule. This is accomplished by condensing the base or the coupling component with an aldehyde or a ketone, as in the analogous condensation of sulphonic acids in the preparation of synthetic tanning agents. Various dyes of this type, e.g.



have been prepared[82], and found to possess high forming and filling power.

An analogous method was suggested at the same time in the German Democratic Republic for the preparation of tanning agents possessing dyeing properties by coupling ordinary diazo-components with phenolic syntans of various types[83].

Dyes exhibiting tanning properties may be of considerable interest in the production of leather for shoe uppers and especially for special types of leather—fancy, garment, glove leathers.

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The production of synthetic tanning agents is at the present time an established branch of fine organic synthesis with a wide range of products intended to replace vegetable tanning extracts and for several purposes of ancillary or special character. The development of this industry in individual countries is determined by the economic conditions, which differ fundamentally.

On the world market vegetable tanning materials, imported predominantly from former colonies or semi-colonial territores, are considerably cheaper than artificial tanning agents. In capitalist countries (especially England and the USA), therefore, the use of substitute syntans on a large scale is not yet justified. Practical interest attaches mainly to their application for special purposes.

The position in the USSR is completely different. Although we have fairly large potential resources of raw materials for the production of tanning extracts, the raw material itself is characterised by a low content of tannins, and is mostly situated in remote, relatively undeveloped regions. Its procurement and transport involve great organisational difficulties and great expense. In the USSR, therefore, vegetable tanning agents are almost twice as dear as the synthetic products. In this situation our most important task is to use syntans to replace vegetable extracts in as large a volume as possible. With an annual demand by the leather industry for ~ 150 000 tons of dry tanning extracts, this provides grounds for developing the manufacture of syntans to the level of a large-scale and economically very efficient branch of the chemical industry.

The possible applications of artificial tanning agents are not restricted to the leather industry. In their structure and physicochemical characteristics these substances are water-soluble polymers, and may find various uses as a special group of such substances. Recent developments in the synthesis of products which combine tanning action with other functions—fixing, dyeing, emulsifying—open up for synthetic tanning agents new prospects of theoretical and practical interest.

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Organophosphorus Complexones

M.I.Kabachnik, T.Ya.Medved', N.M.Dyatlova, O.G.Arkhipova, and M.V.Rudomino

Organophosphorus complexones represent a new class of multidentate reagents. The paper gives a broad survey of methods for the preparation of aminoalkylphosphonic acids, which include the organophosphorus complexones, and their complexing and biological properties are described. The specific characteristics of these complexones are revealed with respect both to certain elements—beryllium, the rare-earth metals, heavy elements, etc.—and with respect to extending the pH range of complex formation. The mode of reaction of organophosphorus complexones is discussed. The bibliography contains two hundred references.

CONTENTS

I. Introduction	503
II. Methods of synthesis	504
III. Complexing properties	507
IV. Biological properties	514

I. INTRODUCTION

An examination of research on complexones[1] leads to the conclusion that the most important tasks of coordination chemistry in general and the chemistry of complexones in particular are problems of the stability of chelates and the selectivity of chelation.

At one time the synthesis and application of derivatives of iminodiacetic, ethylenediaminetetra-acetic (EDTA), cyclohex-1,2-ylenediaminetetra-acetic (CHDATA), diethylenetriaminepenta-acetic (DETAPA), and certain other acids solved the problem of producing a universal complexone that was highly effective for most cations over a definite pH range. Their multidentate character and configurational mobility, enabling them to assume various conformations corresponding to the structural peculiarities of the cations, make these complexones highly effective for many cations. Thus great stability of the chelates was to a considerable extent achieved, but the problems of selectivity of chelation and also those of complex formation in strongly acid and strongly alkaline media still remained unsolved. The necessity thus arose of seeking new complexing reagents.

The production of highly specific reagents is difficult, since such substances should selectively chelate cations which are very closely similar to one another in physical and chemical properties, dimensions, spatial configuration, and tendency to complex formation.

Selective multidentate complexones can probably be prepared in several ways, e.g. by building up a multidentate reagent having maximum geometrical correspondence between the internal ligand profile and the cation, by introducing into the complexone molecule electron-donor atoms and groups which interact specifically with particular cations, or by building up a multidentate reagent able to satisfy the geometrical and donor–acceptor coordination requirements of the ions of one metal while, as completely as possible, not satisfying those of the ions of all other metals. To solve these problems, it is necessary to study the influence of the structural features and the nature of complexones on complex formation and on the selective character of their action. Although consideration of these questions is at present only qualitative, it is to be hoped that the accumulation of data in this field will reveal some quantitative relations.

The chemistry of organophosphorus complexones is one of the new lines of complexone research which will lead to a solution of the above problems. We include in this group those complexones in which carboxyls have been partly or completely replaced by organophosphorus acidic groupings. Whereas the complexing properties of many organophosphorus compounds, mainly extractants (phosphates, phosphonates, and phosphines and their oxides), have been widely investigated[2-8], very little work has yet been done on organophosphorus complexones. The present review systematises published information on their synthesis and properties.

Organophosphorus complexones possess several specific properties which distinguish them fundamentally from their carboxylic analogues and enable several aspects of the selectivity of chelation to be settled. The development of organophosphorus complexones became possible only after methods had been worked out for the synthesis of aminoalkylphosphonic acids, to which group these complexones belong.

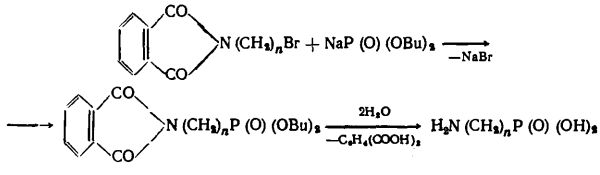
II. METHODS OF SYNTHESIS

The methods available for the preparation of aminoalkylphosphonic acids can be divided into three main groups.

1. Phosphorylation of Substituted Amines

This division comprises methods for the synthesis of aminoalkylphosphonic acids based on the introduction of a phosphonic grouping into an organic amine. The various modifications of these methods usually include either an Arbuzov rearrangement or a Michaelis–Becker reaction. The phosphorylating agents used include sodium dialkyl phosphites, trialkyl phosphites, alkylphosphonous esters, and phosphorus trichloride. In order to prevent side-reactions, the amino-group in the amines is usually blocked by easily removable protective groups.

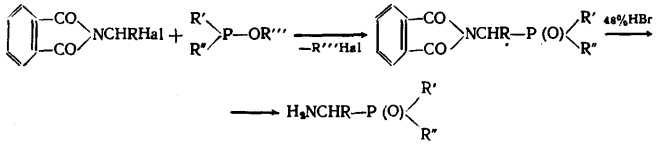
Rumpf and Chavane[9] obtained aminoalkylphosphonic acids by the action of sodium dibutyl phosphite on bromoalkylphthalimides followed by hydrolysis of the resulting phthalimidoalkylphosphonic esters:



where n = 1, 2, 4, 5, 10.

Kosolapoff[10] obtained 2-aminoethylphosphonic acid by the reaction between bromoethylphthalimide and triethyl phosphite.

This method has since been used[11] for the synthesis of α-amino-s-alkylphosphinic acids and α-aminoalkylphosphine oxides. Alkyl- and aryl-phosphonous and -phosphinous esters were subjected to Michaelis–Arbuzov condensation with N-bromomethyl- and N-1-chloroethyl-phthalimides:



where R = H, CH_3; R′ = CH_3, C_2H_5; R″ = C_6H_5, OAlk (OH after hydrolysis); and R‴ = Alk.

ω-Aminoalkylphosphonic esters are formed also by the reaction of bromoalkylamine hydrobromides with sodium dialkyl phosphites (in the proportions 1 : 2 to neutralise the hydrobromic acid liberated[12]):

$$H_2N(CH_2)_nBr\cdot HBr + 2NaP(O)(OR)_2 \rightarrow H_2N(CH_2)_nP(O)(OR)_2 + HP(O)(OR)_2 + NaBr.$$

Owing to the insolubility of hydrobromides in inert anhydrous solvents, however, the yields of the final products are low.

Phosphorus trichloride reacts with alkoxymethylamines to give derivatives of aminomethylphosphonic acid[13-15]†. Thus by adding hydroxymethylamides of aliphatic acids to excess of phosphorus trichloride, Engelmann and Pikl[17,18] obtained the corresponding substituted alkyl phosphorodichloridites $R.CO.NR'.CH_2.O.PCl_2$, which then isomerised into the substituted aminomethylphosphonic dichlorides. Hydrolysis of the latter readily yielded substituted aminomethylphosphonic acids $R'.NH.CH_2.PO(OH)_2$.

Taking the reaction of substituted alkoxymethylamines with phosphorus trichloride as example, Kreuzkamp and Genser showed[19] that this reaction takes place in two stages, with the formation of trialkyl phosphites and chloromethyldialkylamines as intermediate products:

$$PCl_3 + (C_2H_5)_2NCH_2OC_2H_5 \rightarrow (C_2H_5O)_3P + (C_2H_5)_2NCH_2Cl$$
$$(C_2H_5O)_3P + (C_2H_5)_2NH_2Cl \rightarrow (C_2H_5)_2NCH_2PO(OC_2H_5)_2 + C_2H_5Cl.$$

The facility of the first stage is, perhaps, due to the formation of a resonance-stabilised carbonium–immonium cation and an alkoxide anion:

$$R_2NCH_2OR' \rightarrow [R_2\ddot{N}-\overset{+}{C}H_2 \leftrightarrow R_2\overset{+}{N}=CH_2] + R'O^-.$$

In spite of the ease of the synthesis, however, this reaction has not become widely used, since its application is restricted to derivatives of aminomethylphosphonic acid.

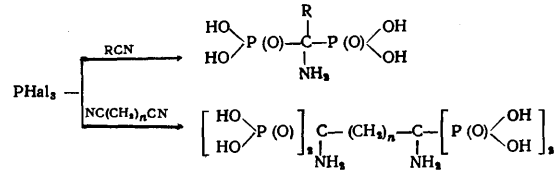
Ivanov and his coworkers have recently shown[20,21] that a similar mechanism is probably involved in the reactions of triethyl phosphite with alkoxymethylamines and with diethylaminoacetonitrile, which also yield diethylaminomethylphosphonic esters:

$$\left.\begin{matrix} R'_2NCH_2OR \\ R'_2NCH_2CN \end{matrix}\right| \xrightarrow[CH_3COOH\ or\ HCl]{(C_2H_5O)_3P} R'_2NCH_2P(O)(OC_2H_5)_2.$$

In contrast to this the reaction between triethyl phosphite and acetamidoacetyl chloride gives an ester of the corresponding amino-α-ketophosphonic acid[22]:

$$RCONHCH_2COCl + (C_2H_5O)_3P \rightarrow RCONHCH_2COP(O)(OC_2H_5)_2.$$

With nitriles and dinitriles phosphorus trihalides undergo a different type of reaction[23,24], yielding in the presence of organic (acetic) and inorganic (phosphorous) acids, on subsequent hydrolysis, the corresponding aminoalkylenepolyphosphonic acids:



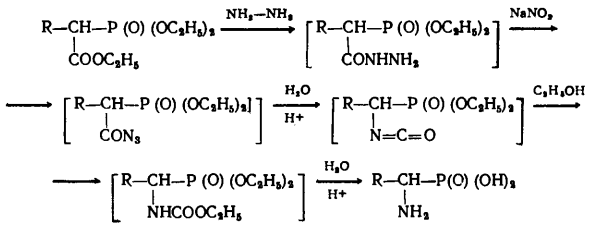
where R = Alk, Ar.

† With white phosphorus alkoxymethylamines give trisaminomethylphosphine oxide, accompanied by aminomethylphosphonic and bisaminomethylphosphinic acids as side-products[16].

2. Amination of Substituted Phosphonic Acids

In most cases classical methods of introducing an amino-group are used for the amination of substances containing a phosphonic group.

Thus by the reaction of α-ethoxycarbonylalkylphosphonic esters with hydrazine Chambers and Isbell[25] obtained the corresponding hydrazides, which after treatment with sodium nitrite and ethanol, followed by hydrolysis with concentrated hydrochloric acid, were converted into α-aminoalkylphosphonic acids in yields of 55–80%. Although the intermediate compounds in this synthesis were not isolated, there is no doubt that the process is a Curtius reaction:



where R = H, CH_3, $CH_2C_6H_5$.

Hydrazoic acid can also be used to convert carboxyalkylphosphonic into aminoalkylphosphonic acids[26]:

$$HOOC(CH_2)_nP(O)(OH)_2 + HN_3 \rightarrow H_2N(CH_2)_nP(O)(OH)_2 + N_2 + CO_2$$

as well as Hofmann decomposition of the amide[27]:

$$(C_2H_5O)_2P(O)(CH_2)_nCOOC_2H_5 \rightarrow (C_2H_5O)_2P(O)(CH_2)_nCONH_2 \xrightarrow{Br_2,KOH,H_2O}$$

$$\rightarrow (C_2H_5O)_2P(O)(CH_2)_nCH_2NH_2 \xrightarrow[H_2O]{H^+} (HO)_2P(O)(CH_2)_nCH_2NH_2,$$

Reaction of α-ketophosphonic acids with mono- and dinitrophenylhydrazines gives the corresponding phenylhydrazones, which can be converted by catalytic hydrogenation into the aminoalkylphosphonic esters[10,28]. Kosolapoff used this method to prepare α-aminobenzylphosphonic acid $C_6H_5.CH(NH_2).PO(OH)_2$.

The addition of amines at a double bond present in a phosphonic acid was described by Pudovik[29] as a case of phosphonoethylation. The reaction is usually conducted in the presence of an alkali metal or an alkali-metal alkoxide[30–33].

The above methods for obtaining aminoalkylphosphonic acids are employed comparatively rarely, since they involve the use of starting materials which are not readily available and are specific for each particular compound, and the more complicated polyaminepolyphosphonic acids cannot be obtained by these reactions. A method which eliminates to some extent these disadvantages is based on the replacement by an amino-group of the halogen in a halogenoalkylphosphonic acid.

Comparison of the kinetics of the replacement of halogen by an amino-group in methyl chloride[34] and in chloromethylphosphonic acid[35] led two of the present Reviewers to the conclusion that the phosphonic group in the latter compound has a deactivating effect on the chlorine atom. In fact, the conversion of iodo- or chloro-methylphosphonic acid into aminomethylphosphonic acid necessitates heating with concentrated ammonia in a sealed tube at 100–120°C,[36,37] and the reaction of 3-bromopropylphosphonic acid with concentrated ammonia to form 3-aminopropylphosphonic acid lasts for 2–3 weeks.[10]; the yields of amino-acids are low (around 20–25%). Still more severe conditions (150–160°C) are required to replace halogen by an amino-group in arylhalogenoalkylphosphinic acids[38].

Halogen present *ortho* to the phosphonic group in an aromatic ring is replaced by an amino-group on treatment with concentrated ammonia under the conditions of the Ullmann reaction, i.e. in the presence of freshly prepared copper(I) oxide[39,40].

Primary and secondary amines react more readily than does ammonia: in strongly alkaline aqueous solution the halogen in chloromethylphosphonic acid is replaced in yields of ~ 50% at only 90–100°C. In many cases, however, mixtures of amines phosphorylated to different extents are formed, and it is frequently difficult to separate them.

In 1949 Schwarzenbach et al. synthesised dihydroxyphosphinylmethyliminodiacetic acid $(HO)_2PO.CH_2.N(CH_2COOH)_2$ and its *N*-methylbetaine $^-OPO(OH).CH_2\overset{+}{N}(CH_3)(CH_2COOH)_2$ by condensing chloromethylphosphonic acid with iminodiacetic and *N*-methyliminodiacetic acids respectively[41].

This acid has been obtained also by condensing aminomethylphosphonic acid with chloroacetic acid[42]. An analogous reaction using chloroacetic acid has been described recently for the preparation of bisdihydroxyphosphinylmethylethylenediaminediacetic acid[43].

Bersworth, Westerback and Martell, and other workers have extended to polyamines the substitution of halogen in a halogenoalkylphosphonic acid by an amino-group. Reaction of the simplest polyamine, ethylenediamine, can in principle be represented by the scheme

$$H_2NCH_2CH_2NH_2 + (n+m)\,ClCH_2PO_3^{2-} + (n+m)\,OH^- \rightarrow$$

$$\rightarrow (^{2-}O_3PCH_2)_mNH_{2-m}CH_2CH_2NH_{2-n}(CH_2PO_3^{2-})_n + (n+m)\,Cl^- + (n+m)\,H_2O$$

where n and m have the values 0, 1, 2.

It has been mentioned above that this reaction is usually accomplished by heating an aqueous solution of a mixture of ethylenediamine and chloromethylphosphonic acid at 90–100°C for several days, the pH of the medium being kept within the range 10–11 by the continual addition of aqueous alkali or sodium carbonate[44–49]. Depending on the proportions of the reactants and the reaction conditions, the product may be predominantly mono-, di-, tri-, or tetra-phosphonic acid. The polyaminepolyphosphonic acids are isolated and purified via their lead salts or by means of ion-exchange resins. Most of the acids have been isolated and identified as their sodium or potassium salts[46–49]. However, it is probably not possible to obtain individual acids in the pure form.

The reaction of chloromethylphosphonic acid with ethylenediamine has been studied in greatest detail by Uhlig and Achilles[50], who have shown that copper(II) salts have a substantial catalytic effect on the reaction. In their presence the duration of the reaction is greatly shortened (from 90–100 to 2–8 h), and preferential formation of the triphosphonic acid can be achieved. These workers isolated and identified ethylenediamine-mono-, -bis-, -tris-, and -tetrakis-methylphosphonic acids.

Besides ethylenediamine, the method has been applied also to alkylenediamines containing 2–6 carbon atoms in the chain[44,47,48,50]; to *N*-alkylated and *NN'*-dialkyl(aralkyl)-ated alkylenepolyamines of the type $RNH.A.[NH.A]_n.NHR$, where R = H, C_2H_5, C_4H_9, $C_{18}H_{37}$, $CH_2C_6H_5$, A = CH_2CH_2, $CH_2CH_2CH_2$, $CH(CH_3).CH_2$, and n = 0–4 [45,51]; to alkylenediaminediacetic acids of the type $HOOC.CH_2.NH.[CH_2]_n.NH.CH_2.COOH$, where n = 2–6;[46] and to alicyclic diamines[49], aromatic amines[52], and mono-, bis-, and poly-hydroxyalkylamines[53–56].

Esters and amides of other chloroalkylphosphonic[57,58] and bischloromethylphosphinic[59] acids also exchange their chlorine for an amino-group.

It has been claimed in a patent[60] that the use of chloromethylphosphonous acid $ClCH_2P(OH)_2$ instead of chloro-

methylphosphonic acid yields alkylenediaminetetrakismethylphosphonous acids $[(HO)_2PCH_2]_2N[CH_2]_nN[CH_2P(OH)_2]_2$.

In most cases it is not possible from patent information to assess the purity of the products, but the wide possibilities of applying this method to the phosphorylation of various polyamines indicate that it is extremely promising.

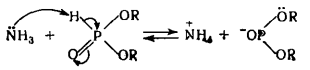
3. Condensation of Dialkyl Phosphites and their Analogues with Amines and Aldehydes or Ketones

In 1952 Kabachnik and Medved' [61,62] suggested a new method for synthesising α-aminoalkylphosphonic acids, which was based on the condensation of dialkyl phosphites with ammonia and a carbonyl compound. The resulting aminoalkylphosphonic esters were saponified to the free acids:

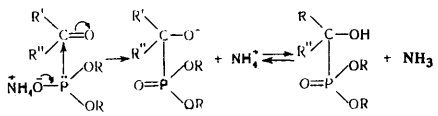
$$(RO)_2PHO + R'—CO—R'' + NH_3 \rightarrow (RO)_2P(O)—\underset{R'\ \ R''}{C}—NH_2 \xrightarrow[H_2O]{H^+} (HO)_2P(O)—\underset{R'\ \ R''}{C}—NH_2 .$$

A little later Fields reported [63] the preparation of esters of substituted α-aminoalkylphosphonic acids by the action of dialkyl phosphites on primary or secondary amines and aldehydes. He was unable to obtain the free acids by saponifying the esters. Although the mechanism of this reaction was not investigated, several suggestions have been made concerning its course.

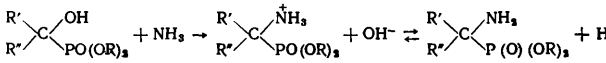
According to Kabachnik and Medved' [64] the first stage in the reaction might be ionisation of the dialkyl phosphite under the influence of ammonia, with migration of the reactive centre and formation of a phosphite anion containing a tervalent phosphorus atom‡:



followed by addition of the phosphite anion to the carbonyl compound:



after which the hydroxy-group is replaced by amino:



To verify this hypothesis, diethyl α-hydroxybenzylphosphonate, obtained by the condensation of diethyl phosphite with benzaldehyde in the presence of a basic catalyst under the conditions of Abramov's reaction [65], was converted by heating with alcoholic ammonia into diethyl α-aminobenzylphosphonate [66].

Another possibility, suggested by Fields [63], consists in the formation of an aminomethanol derivative R_2NCH_2OH as intermediate. Hellmann and Opitz [67] also regard this reaction as a typical α-aminoalkylation.

The first interpretation of the reaction mechanism is supported by its analogy with several well know reactions. In the field of amino-carboxylic acids such a reaction is Rodionov's synthesis—the interaction of aldehydes with ammonia and malonic acid [68]

$$RCHO + NH_3 + CH_2(COOH)_2 \rightarrow RCH_2(NH_2)CH_2COOH + H_2O + CO_2 .$$

In many reactions dialkyl phosphites resemble malonic and acetoacetic esters [69]. Since, however, hydrogen attached to the phosphorus atom plays the part of the reactive methylenic hydrogen, α-amino-phosphonic acids are formed in the present case, in contrast to Rodionov's synthesis (where β-amino-carboxylic acids are formed).

Another closely analogous reaction is Zelinskii's—the formation of amino-nitriles by the action of ammonium cyanide on aldehydes [70]—where the nucleophilic cyano-group is added to the carbonyl group to form a hydroxy-nitrile, which is converted into an amino-nitrile by the action of ammonia§:

$$RCH{=}O + CN^- \rightarrow RCH\langle_{CN}^{O^-} \rightarrow RCH_2\langle_{CN}^{OH} \xrightarrow{NH_3} RCH\langle_{CN}^{\overset{+}{N}H_3} + OH^- \rightleftarrows RCH\langle_{CN}^{NH_2} + H_2O .$$

Ammonium hydrogen sulphite also adds to aldehydes with the formation of α-amino-sulphonic acids [72,73]:

$$NH_4HSO_3 + RCHO \rightarrow RCH\langle_{SO_3H}^{NH_2} .$$

Finally, these reactions resemble the Mannich reaction, the mechanism of which has been vigorously discussed during recent years [67,74,75]. Thus phosphine, organic phosphines, and organic diphosphines react with formaldehyde and amines or with hydroxymethyl derivatives of amines under the conditions of the Mannich reaction to give the corresponding polyaminomethyl-phosphines and -diphosphines [76-79].

A common property of dialkyl phosphites, malonic ester, hydrocyanic acid, and sulphurous acid is their ability to give two series of derivatives. From this it might be supposed that the formation of amino-derivatives of the type $R.CHX.NH_2$ by the action of carbonyl compounds and ammonia is characteristic of all compounds HX which are weak acids and capable of reacting in two ways.

The above reaction was subsequently extended by the same workers to dialkyl thiophosphites [80], diaryl phosphites [81], arylphosphonous esters [64], and diarylphosphine oxides [82], compounds capable of diad tautomerism. The respective products were α-aminoalkylphosphonothioic esters, α-aminoalkylphenylphosphinic esters, and α-aminoalkyldiarylphosphine oxides

$$(RO)_2P(S)—\underset{NH_2}{C}—R'R'' \quad ; \quad \underset{C_6H_5}{RO}\rangle P(O)—\underset{NH_2}{C}R'R'' \quad ; \quad Ar_2P(O)—\underset{NH_2}{C}R'R'' .$$

This method has been developed by Moedritzer and Irani [83], who use phosphorous acid as the phosphorus component. In syntheses with formaldehyde, ammonia, and various amines in strongly acid medium they obtained good yields of a series of α-aminoalkyl-phosphonic and -polyphosphonic acids:

$$R_{3-n}NH_n + n\,CH_2O + n\,HP(O)(OH)_2 \xrightarrow{[H^+]} R_{3-n}N[CH_2P(O)(OH)_2]_n + n\,H_2O .$$

Advantages of this reaction are the absence of a stage in which esters are saponified and the ease with which the products can be isolated.

Just like the phosphorus component, the amine and carbonyl components can also be varied. Hence the condensation of amines and carbonyl compounds with phosphorus compounds can be regarded as the most general method for the synthesis of α-aminoalkylphosphonic acids.

Formaldehyde has been used as the carbonyl component, usually as paraformaldehyde [31,84-86] or 40% aqueous formalin [87-93]. Use has been made also of aliphatic [62,66,95,96], alicyclic [62,95], aromatic [61,63], and heterocyclic [97] aldehydes and ketones. Aliphatic ketones react most readily;

‡ It is probable that complete transfer of the proton does not occur here, but a strong hydrogen bond is formed, which promotes transfer of the proton in the second stage.

§ It is known that hydroxy-nitriles can be converted into amino-nitriles by the action of ammonia [71].

alicyclic and alkyl aryl ketones react with greater difficulty. Purely aromatic ketones (e.g. benzophenone) and aliphatic aldehydes give only low yields of amino-phosphonic esters[95,96].

The range of application of amines—ammonia[61,62,64,66,76,95,97], primary and secondary aliphatic amines[31,63,85,93,94,98], nitrogen heterocycles[31,90], and mono- and bis-hydroxyalkylamines[88]—is also immense.

The interaction of dialkyl phosphites and carbonyl compounds with polyamines yields polyaminebisalkylphosphonic acids, which possess several interesting properties (see Section III). The reaction has been studied on alkylene-diamines[84,89,99,100] and -polyamines containing heteroatoms in a chain of methylene groups[100-102]:

$$2\,(RO)_2PHO + 2\,R'COR'' + H_2NCH_2[CH_2{-}A{-}CH_2]_nCH_2NH_2 \xrightarrow[-H_2O]{}$$
$$\rightarrow (RO)_2P(O)C(R'R'')NHCH_2[CH_2{-}A{-}CH_2]_nCH_2NHC(R'R'')P(O)(OR)_2 \xrightarrow[H_2O]{H^+}$$
$$\rightarrow (HO)_2P(O)C(R'R'')NHCH_2[CH_2{-}A{-}CH_2]_nCH_2NHC(R'R'')P(O)(OH)_2$$

where R = CH_3, C_2H_5, C_4H_9, $CH_2C_6H_5$; R′ and R″ = H, CH_3, C_2H_5, C_6H_5; n = 0, 1; and A = CH_2, O, S, NH.

The present Reviewers and their coworkers have shown that alkylenediaminebisalkylphosphonic esters can be obtained in yields of around 70–80%. The optimum reaction conditions are stoichiometric proportions of the reactants, simultaneous addition of phosphorus and carbonyl components to the polyamine (to avoid side-reactions), and a definite reaction temperature (60°C).[100,103] Hydrolysis of the esters with hydrochloric acid results in several cases in the formation of dihydrochlorides of the acids of general formula

$$[(HO)_2P(O)C(R'R'')NHCH_2CH_2{-}A{-}CH_2CH_2NHC(R'R'')P(O)(OH)_2].2HCl.$$

These are converted into the free acids by treatment with silver oxide or an organic α-oxide[100,101].

It is noteworthy that the condensation of dialkyl phosphites and carbonyl compounds with alkylenediamines yields only diphosphonic acids, in contrast to the reaction of chloromethylphosphonic acid with alkylenediamines (see subsection 2), where mixtures are always obtained of di-, tri-, and tetra-phosphonic acids, the separation of which involves great difficulties.

Apart from the fact that alkylenediaminebisalkylphosphonic acids have been especially interesting complexones of the aminoalkylphosphonic class, the presence of secondary amino-groups enables them to be used to obtain more complicated complexing agents of the phosphonic–carboxylic type. Thus by carboxymethylating ethylenediaminebismethylphosphonic acid we obtained bis-dihydroxylphosphinylmethylethylenediaminediacetic acid[84]:

$$(HO)_2PCH_2NHCH_2CH_2NHCH_2P(OH)_2 \xrightarrow[\text{then HCl}]{NaCN,\ CH_2O,\ NaOH}$$
$$\rightarrow (HO)_2P(O)CH_2\diagdown\!\diagup N(CH_2CH_2N\diagup\!\diagdown CH_2P(O)(OH)_2)\diagdown\!\diagup CH_2COOH \cdot HOOCCH_2$$

Carboxymethylation of diethylenetriamine-*NN*″-bisisopropylphosphonic acid yields *NN*″-bis-(1-dihydroxyphosphinyl-1-methylethyl)diethylenetriamine-*N*′-acetic acid[104]:

$$(HO)_2P(O)C(CH_3)_2NHCH_2CH_2NHCH_2CH_2NHC(CH_3)_2P(O)(OH)_2 \xrightarrow{ClCH_2COOH}$$
$$\rightarrow (HO)_2P(O)C(CH_3)_2NHCH_2CH_2N(CH_2COOH)CH_2CH_2NHC(CH_3)_2P(O)(OH)_2 .$$

A related method is based on the addition of dialkyl (or diaryl) phosphites to Schiff bases, the latter obtained from carbonyl compounds and amines:

$$R{-}CO{-}R' + H_2NR'' \xrightarrow[-H_2O]{} R'\diagdown\!\diagup C{=}NR'' \xrightarrow{(R'''O)_2PHO} (R'''O)_2P(O)C(RR'){-}NHR''.$$

This method permits prior removal of water in the condensation, facilitating in some cases the isolation of the aminoalkylphosphonic esters. This procedure, suggested by Pudovik[105-107], has been applied mainly to aromatic carbonyl compounds and amines, because of the ease with which the corresponding Schiff bases can be obtained[108-112]. Kennedy and Ficken[113] employed this method for synthesising α-aminoalkylphosphonate polymers of the two types

$$\vdots\ \vdots$$
$$(CH_2CHCH_2O)_2P(O)CH(CH_3)NHC_6H_5 \text{ and } (C_6H_5O)_2P(O)CH(CH_3)NHCH_2C_6H_4CHCH_2 .$$
$$\vdots\ \vdots$$

The hydrolysis of the aminoalkylphosphonic esters obtained in this way has not been described, and only when hypophosphorous acid was used were the free acids obtained[114,115]:

$$RN{=}CHAr + H{-}P(H)(=O){-}OH \rightarrow HO{-}P(H)(=O){-}CH(Ar)NHR.$$

The interaction of phosphorous and hypophosphorous esters with alkoxyalkylamines or substituted methylenediamines yields respectively substituted aminoalkylphosphonic[91] and bisaminoalkylphosphinic[116] esters:

$$HP(O)(OR)_2 \xrightarrow{H_2NCH_2X} (C_2H_5)_2NCH_2P(O)(OR)_2$$
$$H_2P(O)OR \xrightarrow{H_2NCH_2X} [(C_2H_5)_2NCH_2]_2P(O)OR$$

where X = $N(C_2H_5)_2$, OCH_3, OC_2H_5. In the case of the lower ($< C_6$) hypophosphorous esters, a mixture of esters of the above two types is usually obtained.

Evdakov and his coworkers have shown that α-aminoalkylphosphonic esters can be formed also by the interaction of dialkyl *NN*-dialkylphosphoramidites with aliphatic and aromatic aldehydes and alicyclic ketones[117,118]:

$$(RO)_2PN(C_2H_5)_2 + R'COR'' \rightarrow (RO)_2P(O)C(R'R'')N(C_2H_5)_2 .$$

A detailed study of this reaction has been made by Hudson et al.[119], who have extended it to arylamides of diphenylphosphinous acid:

$$R_2PNHPh + PhCHO \rightleftharpoons R_2P{-}\overset{+}{N}HPh\ (\text{O{-}CHPh}) \rightleftharpoons R_2\overset{+}{P}H{-}NPh\ (\text{O{-}CHPh})$$
$$R_2\overset{+}{P}H{-}NPh\ (\text{O{-}CHPh}) \rightarrow R_2PO{-}CH(Ph){-}NHPh$$
$$R_2PO{-}CH(Ph){-}NHPh \rightarrow R_2PO^- + Ph\overset{+}{N}H{=}CHPh$$
$$R_2PHO + PhCH{=}NPh \rightarrow R_2P(O)CH(Ph)NHPh \leftarrow R_2PO^- + Ph\overset{+}{N}H{=}CHPh$$

III. COMPLEXING PROPERTIES

The first paper on the complexing properties of aminoalkylphosphonic acids was published in 1949 by Schwarzenbach et al.[41]. Seven years later communications appeared by Martell and his coworkers[47,120] on the potentiometric titration of these acids with metals, followed somewhat later by our own papers[84,99]. However, this early work did not reveal those interesting properties of aminoalkylphosphonic and especially polyaminepolyphosphonic acids which placed them among the most interesting and important of complexones. The most detailed studies of the complexing properties of phosphorylated polyamines have been made during recent years in the laboratories of the present Reviewers in the Institute of Organoelementary Compounds of the USSR Academy of Sciences and the Institute of Chemical Reagents and High-purity Chemicals.

Structural examination of organophosphorus complexones shows that they possess potentialities for complex formation similar to those of their carboxylic prototypes. These substances have the donor functions of the amine nitrogen atoms and the oxygen atoms of the phosphonic group, a tendency to form chelate rings, and the ability to adopt various conformations according to the configurational requirements of metal ions.

Tables 1 and 2 give the stability constants of the complexes for all the phosphorylated polyamines which have been studied up to the present, and also for comparison the stability constants of complexes of certain amino-carboxylic complexones. These data show that amino-alkylphosphonic acids are highly efficient complexing agents, in several cases not inferior to carboxylic complexones. However, in spite of the above similar prerequisites for complex formation, aminoalkylphosphonic acids possess a number of special features.

The specific character of the behaviour of organophosphorus complexones is primarily due to their increased number of donor atoms. The peculiarities of the stereochemistry of the PO_3 group also play an important part. Organophosphorus complexones differ from their carboxylic analogues in exhibiting—(1) preferential complex formation with cations of small atomic radius (beryllium, germanium, iron) and also with cations of large radius, such as the rare-earth elements, (2) diminished complex formation with the alkaline-earth metals, (3) an unusual stability sequence with transition metals, (4) the ability to form stable complexes in the acid pH range, and (5) the ability to form homo- and hetero-dinuclear complexes.

Henceforward in the text we have adopted for convenience the abbreviations for the names of the complexones listed in Table 3.

Table 1. Logarithms of stability constants for complexes of alkaline-earth and transition metals (for abbreviations for complexones see Table 3).

No.	Complexone	Mg^{2+}	Ca^{2+}	Sr^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Fe^{2+}	Ref.
1	EDAMP				2.20	3.20	4.40			2.7			129
					5.16	7.95	9.62	>14		7.60			
2	EDBMP	—	—	—	3.63	3.84	4.71	8.72	5.02			>8	125
		<2	<2	<1	7.55	10.80	12.02	18.58	12.04			>15	
3	EDABIP	—	—	—	3.57	3.84	3.84	8.83	4.81		8.2	>10	125
		<2	<2	<1	8.00	11.19	11.23	20.35	13.38		16.0*	>15	
4	PMDABIP	<2	<2	<1	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	100
5	DETABIP	<1	<1	<1	3.43	4.45	4.98	9.55	5.40	4.65	6.30		100
		<1	<1	<1	9.82	13.86	14.36	19.85	15.60	13.34	17.68		
6	TBEAIP	—	—	—	3.11	2.74	—	5.96	3.75	—	5.40		100
		<3	<3	<3	8.57	10.71	11.39	15.90	12.86	12.70	14.39		
7	OBEAIP	—	—	—	—	—	—	6.30	3.76	4.96	5.65		100
		3.65	5.61	3.97	7.45	9.02	8.84	16.18	11.17	12.04	11.68		
8	EDTMP	5.0	4.95	—	6.99	8.51	9.12	11.14	9.90	8.81		—	126
		8.63	9.33		12.70	15.49	15.30	18.95	17.05	13.88			
			—		—			—				13.2	48
			5.74		9.40			16.09				19.6	
9	CHDATMP	6.41	5.49	3.72	8.42	3.3**	3.93**	9.73	9.12	8.06	7.99	23.3**	49
10	DETAPMP	3.94	4.04	—	5.34	7.35		11.60	8.44	6.36			126
		6.40	7.11		11.15	15.73		19.47	16.45	13.37			
11	PMADA	1.96	2.43	1.63									41
		6.28	7.18	5.59									
		6.00	7.1	5.40	8.0				9.0	8.5			120
12	PEADA	2.14	2.05	1.59									41
		6.33	5.44	4.10									
13	PMAAP				—			7.2					48
			4.88		7.24			13.0				16.3	
14	BPMAA				—			5.44					48
			6.17		7.0			12.53				14.65	
15	BPMEDDA	—	—	3.44	7.0	—	9.49	9.4				>12	125
		8.11	7.91	6.89	13.63	16.03	15.23	18.5	16.85*			>15	
			8.89***	8.31***									124
16	EDDA	3.9				11.2	13.5	16.2	11.1	8.8			199
17	EDTA	2.28	3.51	2.30	0.47	3.09	5.20	5.58	3.28	3.3	5.02		199
		8.69	10.59	8.63	14.04	16.31	18.62	18.80	16.50	16.46	18.04	25.1	
18	NTA	5.41	6.41	4.98	7.44	10.61	11.26	12.68	10.45	9.8		15.9	199

The first line gives values of $\lg K_{st}$ for the hydrogen complexes (MH_2L for acids Nos.2–8 and 15, MH_3L for No.10, and MHL for Nos.11–14 and 17); the lower line gives $\lg K_{st}$ for the normal complexes ML.

* Polarographic data

** Spectrophotometric data

*** Data from ion-exchange chromatography

In the remaining cases, potentiometric data.

1. Acid Dissociation

Among the aminoalkylphosphonic acids which have been investigated, two main groups of substances can be separated, which give metal complexes comparable in stability with—and in some cases even surpassing—the corresponding complexes of amino-carboxylic acids. These groups comprise (1) alkylenepolyaminebis(tris, tetrakis, and pentakis)-alkylphosphonic acids and (2) mixed alkylenepolyaminepoly-alkylphosphonic–polyacetic acids.

From a study of the titration of aminoalkylphosphonic acids with dilute acids and alkalis, Chavane[121] and Schwarzenbach[41] showed that these substances had a betaine structure. This has since been confirmed by

Table 2. Logarithms of stability constants for complexes of the rare-earth metals (for abbreviations for complexones see Table 3.).

Complexone	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Y^{3+}	Ce^{4+}	Ref.
EDBMP	7.49		7.84*	8.31	8.43	8.15*	8.31	8.45	8.79*	8.84	8.92	8.99*	9.44		8.79		125.150
	ppt.		ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.		oc		
EDABIP	5.37		5.79	5.81	6.20	6.18	6	6.40	6.20	6.88	—	—	—	7.66	6.47		125.150
	10.13		10.13	11.59	12.56	12.44	12.27	12.18	12.89	12.11*	13.39	13.34	13.92*	13.37*	12.86*		
PMDABIP	4.44			4.96	5.49		5.49		5.49					6.90		8.72	100
	ppt.			ppt.	ppt.		ppt.		ppt.					ppt.		ppt.	
DETABIP	5.50			5.96	6.50												100
	9.89			12.01	14.01												
TBEAIP	4.83			5.75	5.92		5.92		5.92					6.46		8.40	100
	10.01			10.91	11.80		11.80		11.80					13.03		17.04	
OBEAIP	5.38			5.71	6.01		6.01		6.01					7.11		9.45	100
	11.06			11.04	12.02		13.37		12.04					13.36		17.62	
EDTMP	12.13			13.05	13.68		13.12			13.17		12.88					126
	20.15			21.47	22.39		21.80			21.85		21.41					
BPMEDDA	8.43		9.22	9.45	9.20	9.64*	9.22						9.20	9.20	10.36		125.150
	15.60		16.51	17.56	17.12*	17.80*	17.35	19.10*	17.45	19.02*	20.12*	20.96*	17.65	17.68	18.52*		
		18.51***													24.03***		124
EDDA	7.04		7.84	8.06	8.28	8.38	8.13	8.18	8.31	8.42	8.59	8.75	8.93	9.09	7.78		199
EDTA	3.28			4.39													
	15.50		16.40	16.61	17.14	17.35	17.37	17.93	18.30	18.67	18.85	19.32	19.51	19.83	18.09		199
DETAPA	19.48	20.15	21.17	21.6	22.34	22.39	22.46	22.71	22.82	22.78	22.74	22.72	22.62	22.44	22.05		200

DETAPA = diethylenetriaminepenta-acetic acid

* ** *** As in Table 1.

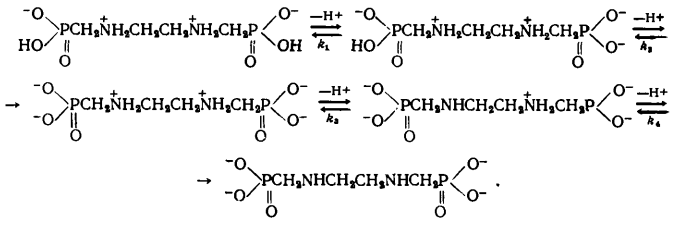
Table 3. Complexones and their abbreviations.

No.	Acid	Formula	Abbreviation
1	Ethylenediaminemethylphosphonic	$H_2NCH_2CH_2NHCH_2P(O)(OH)_2$	EDAMP
2	Ethylenediaminebismethylphosphonic	$(HO)_2P(O)CH_2NHCH_2CH_2NHCH_2P(O)(OH)_2$	EDBMP
3	Ethylenediaminebisisopropylphosphonic*	$(HO)_2P(O)C(CH_3)_2NHCH_2CH_2NHC(CH_3)_2P(O)(OH)_2$	EDABIP
4	Pentamethylenediaminebisisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NH(CH_2)_5NHC(CH_3)_2P(O)(OH)_2$	PMDABIP
5	Diethylenetriamine-*NN''*-bisisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NHCH_2CH_2NHCH_2CH_2NHC(CH_3)_2P(O)(OH)_2$	DETABIP
6	Thiabisethylamineisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NHCH_2CH_2SCH_2CH_2NHC(CH_3)_2P(O)(OH)_2$	TBEAIP
7	Oxabisethylamineisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NHCH_2CH_2OCH_2CH_2NHC(CH_3)_2P(O)(OH)_2$	OBEAIP
8	Ethylenediaminetetrakismethylphosphonic	$[(HO)_2P(O)CH_2]_2NCH_2CH_2N[CH_2P(O)(OH)_2]_2$	EDTMP
9	Cyclohex-1,2-ylenediaminetetrakismethylphosphonic	$C_6H_{10}\{N[CH_2P(O)(OH)_2]_2\}_2$	CHDATMP
10	Diethylenetriaminepentakismethylphosphonic	$[(HO)_2P(O)CH_2]_2NCH_2CH_2NCH_2CH_2N[CH_2P(O)(OH)_2]_2$ (with $CH_2P(O)(OH)_2$ branch)	DETAPMP
11	Dihydroxyphosphinylmethylaminediacetic	$(HO)_2P(O)CH_2N(CH_2COOH)_2$	PMADA
12	Dihydroxyphosphinylethylaminediacetic	$(HO)_2P(O)CH_2CH_2N(CH_2COOH)_2$	PEADA
13	Dihydroxyphosphinylmethylamine-*N*-acetic-*N*-propionic	$(HO)_2P(O)CH_2N(CH_2COOH)(CH_2CH_2COOH)$	PMAAP
14	Bisdihydroxyphosphinylmethylaminoacetic	$[(HO)_2P(O)CH_2]_2NCH_2COOH$	BPMAA
15	Bisdihydroxyphosphinylmethylethylenediamine-*NN*-diacetic	$(HO)_2P(O)CH_2N(HOOCCH_2)CH_2CH_2N(CH_2P(O)(OH)_2)(CH_2COOH)$	BPMEDDA
16	Ethylenediaminediacetic	$HOOCCH_2NHCH_2CH_2NHCH_2COOH$	EDDA
17	Ethylenediaminetetraacetic	$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$	EDTA
18	Nitrilotriacetic	$(HOOCCH_2)_3N$	NTA

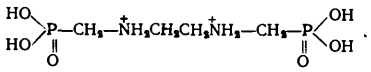
* "Phosphicin" = disodium salt of EDABIP.

results for the infrared spectra[86] and by X-ray examination[122]. Recently Burpitt and Goodlett have shown[123] by means of nuclear magnetic resonance (n.m.r.) that several dimethyl esters of substituted α-aminoalkylphosphonic acids are also internal salts.

For the initial member in the first group of organophosphorus complexones—ethylenediaminebismethylphosphonic acid (EDBMP)[84,101]—the possible stages of dissociation can be represented, according to our results, by the equations



An analogous scheme of dissociation is probably applicable in the remaining cases. In strongly acid media the original betaine is able to take up two protons to form the doubly charged cation



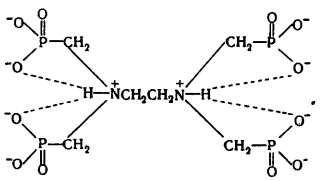
Comparison of the dissociation constants of aminoalkylphosphonic acids of the first group (Table 4) and of analogous carboxylic acids reveals a difference in the properties of these substances. For example, aminoalkylphosphonic acids have values of the latter two dissociation constants,

Table 4. Negative logarithms of dissociation constants of complexones.

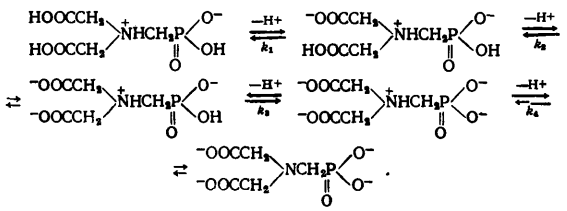
Complexone	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8	pK_9	pK_{10}	Ref.
EDAMP	4.85	7.36	10.25								119
EDBMP	4.61	5.72	8.02	10.47							125
EDABIP	4.95	6.00	8.55	11.68							125
PMDABIP	5.77	6.13	11	11							100
DETABIP	5.39	6.55	10.40	11.20							100
TBEAIP	5.51	6.34	10.38	11.48							100
OBEAIP	5.15	6.40	10.56	11.48							100
EDTMP	1.46	2.72	5.05	6.18	6.63	7.43	9.22	10.60			48
	1	1.5	3.02	5.22	6.40	7.85	9.82	11.00			50
	—	—	3.0	5.23	6.54	8.08	10.18	12.10			126
CHDATMP	2.40	3.70	5.32	6.46	6.97	7.69	9.39	10.89			
DETAPMP	—	—	2.8	4.45	5.50	6.38	7.17	8.15	10.10	12.0	126
PMADA	2.00	2.25	5.57	10.76							41
PEADA	1.95	2.45	6.54	10.46							41
PMAAP	2.72	3.48	5.59	10.41							48
BPMAA	1.73	2.00	5.01	6.37	10.80						48
BPMEDDA	1.5	2.30	4.65	6.16	8.36	10.3					125
	2.0	2.68	5.66	6.12	8.34	10.7					124
EDDA	6.42	9.46									199
EDTA	2.00	2.67	6.16	10.26							199
NTA	1.89	2.49	9.73								199

corresponding to elimination of the betaine protons, which are unusually large but differ relatively little from one another. This is observed especially clearly in the diphosphonic acids as the methylene chain linking the aminoalkylphosphonic groups becomes longer, when the difference in the latter two dissociation constants decreases to factors of $10^{1-0.5}$, which can be explained by the weakening of the inductive effect exerted by one $^+NH_2.C.PO_2^{2-}$ group on the other[101]. Introduction of a heteroatom—nitrogen, oxygen, or sulphur—into the methylene chain has no significant effect on the dissociation constants of the corresponding acids[100].

In the case of tri-, tetra-, and penta-phosphonic acids the decrease in repulsion between the two positively charged nitrogen atoms is probably due partly to the high charge on the anion and partly to electrostatic bonding (a weak hydrogen bond) of the betaine protons to the negatively charged oxygens of the phosphonic groups[48]:



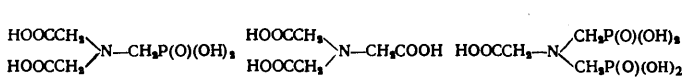
The dissociation constants of the mixed polyamine-polyphosphonic-polyacetic acids are given in Table 4. In view of the difference in basicity between carboxyl and phosphonic acid groups, it may be supposed that in this case the betaine structure is produced at the expense of the hydrogens of the latter groups. Further assignment of the individual dissociation constants of these acids to the successive elimination of carboxylic, the second phosphonic, and then the betaine protons enables the following dissociation scheme to be put forward[41,120,124,125]



2. Effect of Increase in Multidentate Character

It might have been expected that successive replacement of one, two, . . . , and finally all the carboxymethyl groups in polyamino-polycarboxylic acids by dihydroxyphosphinylalkyl groups would be accompanied by a corresponding regular change in the complexing properties of these substances. However, this is not observed.

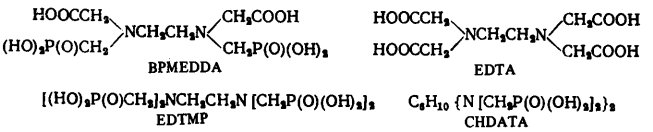
Whereas dihydroxyphosphinylmethylamine-*NN*-diacetic acid (PMADA) gives more stable complexes, both with alkaline-earth metals and with transition-metal ions, than does nitrilotriacetic acid (NTA)[41,120], bisdihydroxyphosphinylmethylaminoacetic acid (BPMAA) gives less stable complexes than does nitrilotriacetic acid throughout a comparable series of metals[48].



PMADA NTA BPMAA

Bisdihydroxyphosphinylmethylethylenediaminediacetic acid (BPMEDDA) forms with copper(II) and the rare-earth elements more stable complexes than does ethylenediaminetetra-acetic acid (EDTA)[124,125], while ethylenediaminetetrakismethylphosphonic acid (EDTMP)[48,126] and cyclohex-1,2-ylenediaminetetrakismethylphosphonic acid (CHDATMP)[49]¶ exhibit weaker complexing powers than do their carboxylic analogues—EDTA and CHDATA.

¶ The stability constants of the metal complexes of CHDATMP seem too low, since they have probably been calculated without regard to the hydrogen complexes [see subsection 3, below].

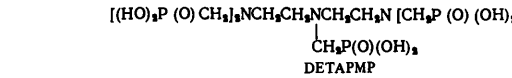


BPMEDDA EDTA

$[(HO)_2P(O)CH_2]_2NCH_2CH_2N[CH_2P(O)(OH)_2]_2$ $C_6H_{10}\{N[CH_2P(O)(OH)_2]_2\}_2$

EDTMP CHDATA

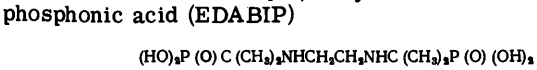
Moreover, the increase in the number of dihydroxyphosphinyl groups on passing from EDTMP to DETAPMP (diethylenetriaminepentakismethylphosphonic acid)



DETAPMP

somewhat diminishes the stability of the complexes formed with alkaline-earth and transition metals, only those with the rare-earth elements constituting an exception[126].

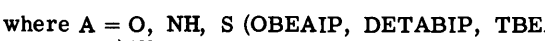
The opposite situation is found with polyaminediphosphonic acids: for example, ethylenediaminebisisopropylphosphonic acid (EDABIP)



EDABIP

not only surpasses in efficiency of complex formation its corresponding ethylenediaminediacetic acid (EDDA), but with copper(II) even surpasses EDTA[125].

Thus the replacement of one carboxymethyl by a dihydroxylphosphinylalkyl group increases the complexing power of the compound, whereas the attachment of more than one of the latter groups to the same nitrogen atom diminishes the efficiency of complex formation. Martell and his coworkers[48] attribute this to the fact that, from steric considerations, two dihydroxyphosphinyl groups attached to one nitrogen atom cannot both take part in coordination, while their high negative charge still more impedes complex formation with cations bearing a low charge (2+). Therefore the conditions are more favourable to cations bearing a high charge. It is possible on the basis of this hypothesis to explain the high stability constants of the complexes formed by iron(III) with the compounds EDTMP, CHDATMP, and EDABIP[48,49,125] and by the rare-earth elements(III) with all the aminoalkylphosphonic acids investigated[124-127], and also the enhanced stability, even in comparison with trebly charged rare-earth elements, of the complexes of cerium(IV) with the compounds

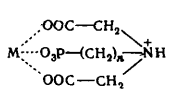


where A = O, NH, S (OBEAIP, DETABIP, TBEAIP respectively)[100].

3. Hydrogen Complexes

A characteristic feature of organophosphorus complexones is their ability to form, besides the normal complexes, stable complexes with metal ions in the pH range preceding the dissociation of the betaine protons. These are termed "hydrogen" or "acid" complexes.

The existence of such complexes was established by Schwarzenbach et al.[41] for the complexes of aminoalkylphosphonic-diacetic acids with alkaline-earth metal ions. These workers attributed to the complexes the structure



and made special mention of the absence of a metal-nitrogen bond in such a complex.

It has since been shown[48,100,125,126] that all polyamine-polyphosphonic acids form in the acid pH range very stable hydrogen complexes with ions of transition metals and rare-earth elements, as well as with bismuth (III), arsenic(III), antimony(III), titanium(IV), tin(IV), and molybdenum(VI) (polarographic data)[128]. Even pentamethylenediaminebis-isopropylphosphonic acid (PMDABIP, A = CH_2), which is a weak complexing agent owing to the great distance between the 1-dihydroxyphosphinyl-1-methylethylamino-groups, nevertheless in the acid pH range gives complexes with rare-earth elements having stability constants[100] of the order of 10^5–10^8.

It is especially noteworthy that in several cases the acid complexes of phosphorylated polyamines are comparable in stability with the normal complexes of amino-carboxylic analogues. Thus rare-earth elements form with EDABIP acid complexes of the same order of stability as the normal complexes they form with EDDA.

Further, unlike the complexes of amino-polycarboxylic acids, the normal complexes of EDTMP and DETAPMP (ML) and their mono-, di-, and tri-protonated complexes (MHL, MH_2L, and MH_3L) are closely similar in stability[126].

Elements having a coordination number of 8 (rare-earth elements, thorium) form stable hydrogen complexes having the composition $M(H_2L)_2$.[125]

The hydrogen complexes formed by beryllium with aminepolyphosphonic acids will be discussed below.

4. Dependence of Stability of Complexes on Position of Metal in Periodic Table

(*a*) Alkaline-earth metal complexes. Amino-alkyl-mono- and -di-phosphonic acids form relatively unstable complexes with alkaline-earth metals, their stability constants not usually exceeding 100.[100,125] With acids containing four or five dihydroxyphosphinyl groups (EDTMP, CHDATMP, DETAPMP), however, the stability constants increase to $10^3(Sr^{2+})$–$10^8(Mg^{2+},Ca^{2+})$.[48,49,126]

The introduction of carboxymethyl groups tends to promote complex formation with alkaline-earth metals, and the complexes of mixed aminoalkylphosphonic–acetic acids with these metals are only slightly less stable than those of the corresponding carboxylic analogues[41,48,100,120,124,125].

(*b*) Transition-metal complexes. The introduction of one dihydroxyphosphinylmethyl group into the ethylenediamine (EDA) molecule—giving ethylenediaminemethylphosphonic acid $NH_2CH_2CH_2NHCH_2PO(OH)_2$ (EDAMP)[129]—increases the complexing power towards transition metals, but not so much (Table 5) as might have been expected from the probable closing of two chelate rings.

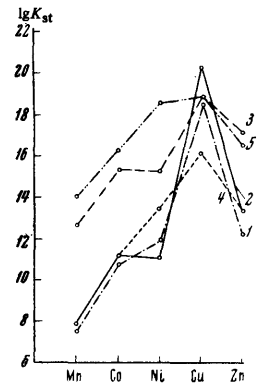
With metal ions whose 3*d*-level is almost complete, aminepolyphosphonic acids form complexes comparable in stability with those of the corresponding aminepolyacetic acids. Irving and Williams[130] established experimentally the sequence

$$Mn<Fe<Co<Ni<Cu>Zn$$

confirmed by Yatsimirskii[131] on the basis of crystal-field theory, for the stability of complexes formed by bivalent transition metals with polyamines and most of the analogues of EDTA. Although, as the accompanying diagram shows, the general variation in stability of the complexes is about the same for these compounds and for phosphorylated derivatives of polyamines, different curves are obtained in the two cases for the variation in the logarithm of the stability constant of the complex with the atomic number of the transition metal. With the phosphorylated derivatives of polyamines the nickel complexes are usually less stable than those of cobalt and zinc, differing in stability constants in the latter case always by factors of 10^2–10^3.

Table 5. Logarithms of stability constants of transition-metal complexes (metal : ligand ratio = 1 : 1).

Metal	EDAMP	EDA
Mn^{2+}	5.16	2.63
Co^{2+}	7.95	5.89
Ni^{2+}	9.62	7.66
Cu^{2+}	~14	10.66
Cd^{2+}	7.60	5.47



Graphical dependence of logarithm of stability constant for transition-metal complexes on the atomic number of the element for the complexones:
1) EDBMP; *2*) EDABIP; *3*) EDTMP; *4*) EDDA; *5*)EDTA.

An especially noteworthy feature is the considerably greater difference than usual between the stability constants of corresponding complexonates of copper and of other transition metals. The stability constants of the copper complexes of the alkylenepolyaminebisalkylphosphonic acids EDABIP, OBEAIP, and DETABIP vary between 10^{18} and 10^{20}, exceeding those of the nickel complexes by factors of 10^8–10^9,[100,125] which is quite exceptional in comparison with the complexes of polyamino-polycarboxylic acids. Whereas most transition metals form less stable complexes with the acids investigated than with EDTA, the copper(II) complex of EDABIP is more stable than the corresponding EDTA complex by a factor of 10^2.[125]

Unusual behaviour is shown by EDABIP towards iron(III). By forming a soluble complex in the pH range in which the betaine proton undergoes dissociation, iron (in fivefold excess) is not precipitated even in the presence of ten equivalents of alkali. The solution changes colour from pale yellow to wine red, gradually passing into a colloidal sol, and then into a gel[125]. This can probably be explained

by the formation in solution of a polycyclic chelate compound of polymeric type, in which cross-linkage occurs through hydroxide ions.

Stable complexes with iron(III) are formed also by EDTMP [48] and CHDATMP. [49] The extraordinarily high stability of the iron(III) complex of the latter acid in comparison with the complexes formed by other metals enabled Banks and Yerick to titrate iron in the presence of a large variety of cations (alkaline-earth metals, Al^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Ti^{4+}, Cr^{3+}, Be^{2+}, etc.)[49].

(*c*) Rare-earth metal complexes. The potential ability of aminoalkylphosphonic acids to increase their multidentate character by means of the oxygen atoms of the dihydroxyphosphinyl groups favours their formation of complexes with the rare-earth metals, which are known to be characterised by a high coordination capacity and a strong affinity for oxygen.

Alkylenepolyaminebisalkylphosphonic acids form complexes with rare-earth metals whose stability constants exceed by factors of 10^3–10^4 those for the corresponding complexes of EDDA [100,125,127]. In the case of EDBMP, which forms water-insoluble complexes, this difference would apparently be still larger, in view of the fact that even the acid complexes of this complexone with rare-earth metals are more stable than the normal complexes of EDDA. [125]

A still stronger complexing action on rare-earth metals was exhibited by EDTMP. Although in the acid pH range (up to five equivalents of alkali) it forms water-insoluble complexes having the composition $M_4(H_4L)_3$, the normal complexes, which are soluble in water at higher pH values, are far more stable than the corresponding complexes of EDTA, and are not inferior in stability to the complexes of diethylenetriaminepenta-acetic acid (DETAPA), which is regarded as the "champion" for complex formation with rare-earth metals [126]. It has been shown also that, in the presence of excess of a rare-earth element, EDTMP forms in the alkaline range soluble polynuclear complexes in which the proportions of metal to complexone are 2 : 1, whereas DETAPMP forms 3 : 1 complexes [126].

Note must be taken also of the masking power for the rare-earth metals exhibited by all the organophosphorus complexones studied [132].

(*d*) Beryllium(II) complexes. Complex formation with beryllium is especially interesting. It has been established that beryllium forms stable complexes with organophosphorus complexones, and this is most specific of the latter, distinguishing them fundamentally from their carboxylic analogues.

Potentiometric titration of mixtures of beryllium(II) and EDABIP (H_4L) in various proportions shows that, in the range preceding titration of the betaine hydrogens, homodinuclear complexes Be_2H_2L and intermediate mononuclear complexes BeH_2L are formed in solution [133].

Neither increasing the distance between the dihydroxyphosphinylalkyl groups as in PMDABIP nor replacing the middle methylene group in the latter by oxygen (OBEAIP) or sulphur(TBEAIP) makes any fundamental change in complex formation with beryllium compared with EDABIP. [134]

When carboxymethyl groups are introduced into an organophosphorus complexone, as in BPMEDDA, complexes are formed with beryllium only after two protons have been titrated. Both this and the fact that the corresponding BeH_2L and Be_2H_2L complexes are closely similar in stability to the corresponding complexes of the above diphosphonic acids probably indicate that the carboxymethyl groups are not involved in the coordination of beryllium [134]. It is interesting that this complexone masks beryllium from precipitation by hydroxides, which constitutes the first case of the masking of beryllium by a complexone [132].

The stability constants of the beryllium complexes, calculated for the monomeric compounds, are given, together with the solubility products of the insoluble complexes, in Table 6.

Table 6. Logarithms of stability constants and solubility products K_s for beryllium(II) complexes.

Complexone	BeH_2L		Be_2H_2L	
	K_s	$\lg K_{st}$	K_s	$\lg K_{st}$
EDBMP	$(2\pm1)\cdot10^{-12}$	8.76	$(3\pm1)\cdot10^{-14}$	11.4
EDABIP	—	7.65	—	11.39
PMDABIP	—	6.15	—	11.21
OBEAIP	—	7.34	—	12.46
TBEAIP	—	7.15	—	11.97
BPMEDDA	—	7.15	$(3\pm1)\cdot10^{-12}$	11.64

In the pH range corresponding to titration of the betaine hydrogens in the free acids, hydroxo-complexes BeH_2LOH and $Be_2H_2L(OH)_2$ are formed in all the cases mentioned, no complexes containing a beryllium–nitrogen bond being produced. This is confirmed also by the identity of the titration curves for beryllium with methyl-, chloromethyl-, and aminoisopropyl-phosphonic acids [135] and the high stability constants of the beryllium complexes of polymethylenediphosphonic acids not containing nitrogen atoms in the polymethylene chain (Table 7) [136].

Table 7. Solubility product and logarithms of stability constants for beryllium(II) complexes of alkylenediphosphonic acids.

Acid	BeL		Be_2L	
	K_s	$\lg K_{st}$	K_s	$\lg K_{st}$
Methylenediphosphonic	—	8.82	—	19.15
Hexamethylenediphosphonic	$(5\pm2)\cdot10^{-13}$	6.31	$(6.6\pm4.0)\cdot10^{-19}$	15.5

The fact that not all the donor atoms of a ligand take part in complex formation makes possible the coordination of another cation. In fact the formation of bimetallic heteronuclear complexes has been established in the polarographic investigation of complicated beryllium complexonate–metal ion (Ca^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) systems [133]. This is confirmed also by the correlation (Table 8) between the dependence of the logarithm of the stability constant of the complex ML and that of the pH at which beryllium is precipitated from a polyheteronuclear complex on the atomic number of the second metal present in the complex. A rough calculation showed [133] that the stability constants of the polynuclear complexes exceed those of the complexes ML by factors of 10^2–10^3 (Table 8).

5. Effect of Heteroatoms on the Stability Sequence of Metal Complexes

The presence in a complexone molecule of heteroatoms—nitrogen, oxygen, sulphur—which tend to coordinate with metals, produces some selectivity with respect to certain cations. Thus for the alkaline-earth metals the relative order of stability is O > N > S, for transition metals containing almost complete *d*-orbitals it is N > S > O, and for rare-earth elements it is O > N > S.

Table 8. Logarithms of stability constants for complexes of transition metals with OBEAIP and pH for hydrolysis of beryllium from the corresponding polynuclear complexes.

Complex	M^{2+}	$\lg K_{st}$ ML	pH of hydrolysis
Be^{2+}	—	—	6.3
$BeH_2L(OH)_2$	—	—	8.3
$BeML(OH)_2$	Ca	5.1	8.2—8.3
	Mn	10.19	8.1—8.2
	Fe	10.90	7.9—8.1
	Co	11.44	7.7—7.9
	Ni	13.13	7.5—7.7
	Cu	18.33	6.4—6.6
	Zn	13.11	7.4—7.6

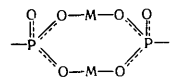
Complex formation by the phosphonic analogues of such complexones has been investigated on alkylenepolyaminebisisopropylphosphonic acids containing oxygen, a secondary amino-group, and sulphur as heteroatom (OBEAIP, DETABIP, and TBEAIP), and also on PMDABIP), in which a methylene group which is definitely incapable of complex formation acts as a quasi-heteroatom [100]. With the phosphorylated derivatives of polyamines as well, the heteroatoms were shown to coordinate to metal ions, but their effect is not so great as, and the stability sequence of the complexonates is somewhat different from, those with the polyamino-polycarboxylic acids: for the alkaline-earth metals the order is O > S > N, for the transition metals N > S > O, and for the rare-earth metals it is N > O > S. In the case of DETABIP (nitrogen as heteroatom) a large difference has also been established in the stability of the complexes from element to element in the rare-earth metals, and hydrogen complexes of more than one type are formed by the elements from gadolinium onwards.

6. Structure of the Complexes

There are still very few studies of the mechanism of coordination of metal ions by phosphorylated polyamine derivatives, the reasons for the specific character of their action, the role of the phosphonic group in complex formation, and other problems.

The structure of complexes of aminepolyphosphonic acids in which coordination of the metal by nitrogen atoms is absent (hydrogen complexes, beryllium complexes, etc.) can be explained by two alternative hypotheses—(1) formation of a four-membered ring

in which the metal ion is coordinated by two of the three oxygen atoms of the phosphonate group, and (2) formation of an eight-membered ring



in which two metal ions are coordinated with four oxygen atoms of two phosphonate groups. Let us examine these postulates in greater detail, noting that neither structure is to be regarded as universally applicable to all metal ions.

1. Four-membered rings were once regarded as unstable and of rare occurrence in the chemistry of complex compounds. However, recent investigations have shown [141-145] that such rings can be formed with metal ions not only by sulphonate, carbonate, and dithiocarbonate groups but also by nitrate, trifluoroacetate, and triazen groups. It has been concluded from these investigations that polyatomic ligands in which two chemically equivalent atoms are situated closer together than are a pair of mutually independent atoms exhibit a tendency to operate through both equivalent atoms, in such a way that the middle position of this pair is located approximately at a vertex of one of the usual coordination polyhedra (octahedron or tetrahedron) [146].

In relation to phosphonate groupings this situation could be interpreted in terms of coordination of the metal ion by two oxygen atoms in each phosphonate group, in such a way that the ligand field would have a roughly tetragonal (octahedral or tetrahedral) configuration; the oxygen atoms, however, do not lie at vertices of the corresponding polyhedron, but form a new distorted polyhedron in which the coordination number of the metal is higher than usual. It is quite difficult to say anything *a priori* concerning the possible spatial configurations which are produced in this case, probably a dodecahedron or distorted antiprism type of configuration. However, it is not excluded that in certain cases the two oxygen atoms of the phosphonate group will occupy two coordination sites in the usual way [147-149].

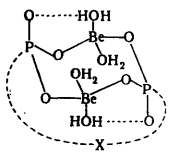
The suggested mechanism [150] provides an explanation not only for the existence and stability of the hydrogen complexes but also for several other features of complex formation by organophosphorus complexones. It suggests that, in normal complexes in which hydrogen atoms are involved in coordination, structures can be produced in several cases having additional four-membered rings, together with the usual structures in which only one oxygen atom of each phosphonate group takes part in coordination, similarly to carboxyl oxygen [151-154]. It is possible that the enhanced stability of complexes formed by phosphorylated polyamines with copper(II), lead(II), and the rare-earth metals is due to the formation of such structures strengthened by additional rings.

A very likely possibility is the formation of complexes, whose structure contains four-membered rings the phosphonate oxygens of which lie at the corners of polyhedra, with metals having a large covalent radius, e.g. uranyl UO_2^{2+} and zirconium(IV). [155,156] In fact it has recently been observed that phosphorylated polyamines exhibit special affinity for uranium in particular [157].

2. The hypothesis of eight-membered bridging rings of the type indicated above has been used by Block and his coworkers to explain the structure of the polymeric tetrahedral complexes formed by Co^{2+}, Zn^{2+}, Be^{2+}, and Cr^{3+} with dimethyl-, diphenyl-, and methylphenyl-phosphinic acids R_2POOH. [158-160] The probable existence of such structures has been confirmed by infrared spectroscopy [161-163]

and X-ray examination[164] for compounds such as the polymeric $\{[R_2PO_2]_nCo\}_n$ and the dimeric $[(C_6H_5)_2PO_2]_2 \cdot [Co(CH_3COCHCOCH_3)_2]$ [sic†].

Kabachnik et al. have suggested this type of structure for the beryllium complexes of alkylenepolyphosphonic and alkylenepolyaminebisalkylphosphonic acids[134,136]. The improved stability of such complexes in acid medium is attributed to stabilisation of the molecule as a whole by internal hydrogen bonds formed by coordinated water molecules and the phosphonate oxygen atoms in a similar manner to that suggested for phosphate complexes[165] and ammines of metal acetates[166,167]. Thus the complex Be_2H_2L (where H_4L = EDABIP, OBEAIP, TBEAIP) is probably built up in such a way that each beryllium ion is coordinated by two oxygen atoms from different phosphonate groups, while the hydrogen bonds form two additional six-membered rings:



Calculations show that the stabilising hydrogen bond should be strong, the O...O distance being around 2.5–2.6 Å.

The above discussion shows that investigation of the efficient and highly selective group of organophosphorus complexones is still far from complete. A series of questions should be studied. Thus the mechanism of complex formation by the phosphonate group and the nature of the selectivity of its action remain obscure. More complete data must be obtained on the dependence of the complexing power of aminepolyphosphonic acids on the position of a metal ion in the Periodic System, and the reasons for the departure from the order of the Irving–Williams series explained.

However, several practical applications are already being planned for this group of complexones. Because of their selective action, phosphorylated polyamines can be successfully used for the fractional determination of cations present in difficultly separable combinations. The great difference in stability of complexes of polyaminepolyphosphonic acids with transition metals and with rare-earth metals, and also the formation with the rare earths of soluble and insoluble complexes exhibiting a quite large difference in stability constants, not only enable the rare-earth elements to be separated from transition metals but also hold out the promise of separating pairs of rare earths lying close together. Complex formation by aminoalkylphosphonic acids in acid medium opens up wide possibilities in work with readily hydrolysable salts. The high stability constants of the complexes formed by several of the above complexones with copper(II) and iron(III) make them promising both for the treatment of copper and iron chloroses of plants in agriculture and for cleaning and passivating surfaces in power engineering equipment[168].

Monoesters of α-anilinobenzylphosphonic acid can be used for the extraction of metals from aqueous solutions[169]. Patents have been taken out for the use of aminoalkylphosphonic and aminoalkylphosphonous acids to soften water[23,24], to prevent the decomposition of peroxy-compounds (by combining with copper(II) ions, which catalyse the oxidation), to remove rust marks from metal structures[24], for the chelation of rare-earth and heavy metals[35,36], to prevent the precipitation of aluminium hydroxide during the etching of aluminium and its alloys[170], as nematocides and soil fungicides[60], as additives to lubricating oils[45,94], etc.

IV. BIOLOGICAL PROPERTIES

Until recently information on the biological properties of aminoalkylphosphonic acids was confined to a few disconnected publications concerned with the search for bacteriostatic preparations.

Although aminoalkylphosphonic acids can be regarded as phosphorus analogues of amino-carboxylic acids, which form part of vegetable and animal organisms, for a long time nothing was known of their occurrence in Nature. It was only in 1959 that Horiguchi and Kandatsu were able[171-172] to isolate from *Rumen protozoa* 2-aminoethylphosphonic acid $NH_2CH_2CH_2PO_3H_2$, which was given the name ciliatin‡. This was the first example of the occurrence in biological materials of a compound containing a carbon-phosphorus bond. Ciliatin and its ester with glycerol have since been detected also in bacteria of the type *Tetrahymena*[173-175], in the sea-anemone *Anthopleura elegantissima*[176], and in *Metridium dianthus*[177]. The crystal structure of ciliatin has been elucidated by Okaya[122] by X-ray structural analysis. A mechanism for the production of ciliatin in biological systems has been suggested recently by Segal[178].

In the course of the investigation of aminoarylphosphonic acids as possible analogues of sulphonamide preparations it was found that phosphanilic (*p*-aminophenylphosphonic) acid and some of its analogues possess bactericidal properties[179-184], while aminomethylphosphonic acid suppresses tobacco mosaic virus[185]. This last compound and several other aminoalkylphosphonic acids can retard the growth of the silkworm and the chick embryo, although they are not natural metabolites of these organisms[185]. It has been found also that in protein synthesis aminomethylphosphonic acid diminishes the inclusion of methionine[186]. No fundamental practical advance was made on these lines of investigation.

A systematic study of the biological properties of aminoalkylphosphonic acids was undertaken in connection with the synthesis of polyaminepolyalkylphosphonic acids and the elucidation of the specific character of their complexing properties, when possibilities were opened up for using substances of this type to treat metal poisoning in humans. Broad biological investigations of organophosphorus complexones are being conducted at the present time in the Institute of Industrial Hygiene and Occupational Diseases of the USSR Academy of Medical Sciences by one of the present Reviewers and his collaborators. It has been found[187] that derivatives of 1-amino-1-methylethylphosphonic acid, applied parenterally as the sodium salts, are tolerated in large doses by animals (mice, rats, guinea-pigs, and rabbits). Thus LD_{min} of sodium ethylenediaminebisisopropylphosphonate (the corresponding medicinal preparation is "phosphicin") is 6 g kg^{-1} for rats and mice. The absence of hypocalcaemia among the animals' symptoms, as a consequence of the low stability constant of the calcium complex, has enabled the sodium salts of these acids to be used even in large doses. Prolonged repeated injections of phosphicin did not affect the increase in weight of animals, the threshold of nervomuscular excitability to electrical stimuli, or the blood pressure, nor did they disturb the functioning of the

† The reference quoted deals with such polymeric compounds of chromium(III) which contain a $(CrOPO)_2$ bridge structure (Ed. of Translation).

‡ This name does not appear to be used in the reports in English on this material (Ed. of Translation).

kidneys or the ability of the liver to render noxious substances harmless. In animals no changes were observed in the peripheral blood. Phosphicin did not change the activity of hydrolases acting on ester bonds (EC.3. 1,.

Experiments with ^{14}C-phosphicin showed that the preparation was completely eliminated two days after parenteral introduction. After one day the urine shows its maximum activity, but a considerable proportion of the preparation is eliminated by the intestines. After ^{14}C-phosphicin has been introduced *per os*, a larger proportion of it is excreted by the intestines [188]. The effect of phosphicin on the metabolism of calcium has been examined in detail. Experiments with ^{45}Ca showed that no danger of hypocalcaemia arose on the introduction of phosphicin [188]. This distinguishes phosphicin fundamentally from polyaminepolyacetic acids, which cannot be applied as their sodium salts owing to the hypocalcaemia which they produce [189]. The relative instability of the calcium complexonates is an important property of polyaminediphosphonic acids, since, as a consequence of the high concentration of calcium in the blood, this cation competes, for a position in the complex, with any metal introduced into the organism.

The effectiveness of amino-polycarboxylic acids in the organism is determined not only by the stability of the complexonate of the metal to be eliminated but also by the ability of this metal to displace calcium from the complex. The position of equilibrium in the process of complex formation in the organism therefore depends on the relative stability constants of the complexonates of the metal and of calcium. This situation is of no fundamental significance with polyaminediphosphonic acids because of the relative instability of their calcium complexes, which has been the chief condition for the use of organophosphorus complexones in biology and medicine.

Experimental investigations have shown the usefulness of employing phosphicin to accelerate the elimination of lead from the organism [190]. It is found that lead is excreted not only by the kidneys but also to a considerable extent by the intestines, which has allowed this preparation to be applied more widely not only in the wards but perhaps also under outpatient conditions for medicinal and prophylactic purposes.

The ability of aminepolyphosphonic acids to form stable complexes with copper increases the elimination of this metal from the organism, and opens up the possibility of using them in the treatment of hepatocerebral dystrophy [191].

The formation of stable water-soluble complexes with beryllium has suggested the use of organophosphorus complexones to accelerate the elimination of this element from the organism [191-193]. Whereas amino-polycarboxylic acids have no effect on the course of acute poisoning by salts of beryllium or on its elimination from the organism, aminepolyphosphonic acids—in particular phosphicin, diethylenetriamine-*NN*″-bisisopropylphosphonic acid, and oxabisethylaminoisopropylphosphonic acid—protect animals from death on introduction of absolute lethal doses of beryllium chloride. The animals do not develop the dystrophic and necrobiotic changes in the internal organs which are characteristic of beryllium poisoning [192]. The protective effect of the complexones is explained by the formation in the organism of a non-toxic water-soluble beryllium complex which is rapidly eliminated from the organism. Experiments with $^{7}BeCl_2$ have shown that the increased excretion of beryllium from the organism results in a decrease in its content in the bones, liver, kidneys, spleen, and lungs [191-193]. The thoroughness of the eliminating effect of organophosphorus complexones is indicated also by the normalisation of the metabolic disturbances caused by beryllium. Thus phosphorylated polyamines reactivate in considerable measure the orthophosphate monoester phosphohydrolase (EC. 3.1.3.1.), and bilirubinaemia is diminished [191]. The action of phosphicin is strengthened by the simultaneous introduction of sodium nitrate, pyridoxin, and glucuronic acid [192]. The effectiveness of organophosphorus complexones in eliminating beryllium from the organism makes them promising as drugs and preventives in beryllosis, one of the most serious occupational diseases.

There are indications that diethylenetriaminepentakismethylphosphonic acid may be effective in relation to uranium [157].

The partial replacement by phosphonate groups of the carboxylate groups in a complexone molecule has been shown to improve the effectiveness of the compound obtained. Thus the introduction of bisdihydroxyphosphinylmethylethylenediaminediacetic acid into animals causes enhanced elimination of yttrium-91 and cerium-144. However, the use of compounds in which carboxylate groups have been completely replaced by phosphonate groups led to a greater accumulation of these radioactive elements in the organism than did the amino-polycarboxylic acids [194].

Data on the influence of complexing compounds on the elimination of trace elements from the organism and on the state of biocomplexes are of both theoretical and practical interest [195-198]. The possibility of complexones, including organophosphorus complexones, acting in this way is due to the high stability constants of the complexonates of copper, iron, cobalt, zinc, etc. Aminepolyphosphonic acids, when introduced into the organism, combine with trace elements and thus enter into competition with the biocomplexes of the organism, the result of this interaction depending on the strength of bonding of the trace elements with the biocomplexes. If a complexone acts on a metal whose link in the biocomplex is labile, as occurs in glycylglycinehydrolase (EC.3.4.3.1), the metal may be removed and the functions of the enzyme disturbed. In the case of the true metal enzymes, such as cytochrome $C-O_2$ oxidoreductase (EC. 1.9.3.1), and cytochrome C, the complex does not break down, as is indicated by the preservation of the haem structure [191].

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Structure of Organic Oxygen Compounds of Sulphur

Yu.A.Kolesnik and V.V.Kozlov

The nature of the sulphur-oxygen bond, the geometry of molecules of the types XYSO, $XYSO_2$, XSOOH, and XSO_2OH, and the character of the intramolecular interactions in these compounds are discussed. Apart from the σ-bond between sulphur and oxygen, interaction obviously occurs by means of the $3d$-orbital of sulphur and the $2p$-orbital of oxygen ($2p$-$3d$ hybridisation). The interaction of a sulphinyl group with the substituents X and Y is not conjugation, but has an induction and electron-acceptor character.

In all oxygen compounds of sulphur the sulphonyl group has a tetrahedral structure with the sulphur atom at the centre of the tetrahedron, in good agreement both with the chemical properties and with the assignment of the modes of vibration of sulphur-oxygen bonds in infrared and Raman spectra. The position ν_{SO} of the stretching bands is affected only by change in the character and length of the sulphur-oxygen bond with variation in the electronegativity of the substituents X and Y or on passing from ionised to covalent compounds. These properties of the ν_{SO} absorption bands are explained by the highly specific character of the sulphur-oxygen vibrations. The bibliography contains 139 references.

CONTENTS

I. Introduction 519
II. Groups containing a sulphur-oxygen bond 519
III. Infrared spectra of oxygen compounds of sulphur 523
1. Appearance of sulphur-oxygen bond in infrared spectra 523
2. Factors affecting position of sulphur-oxygen stretching bands 526
3. Relation between sulphur-oxygen stretching frequencies and parameters of the sulphur-oxygen bond 529
4. Intensity of ν_{SO_2} bands 529

I. INTRODUCTION

The sulphonation of organic compounds is widely used in the manufacture of many industrial products. The introduction of a sulpho-group SO_2OH into an organic molecule confers on the resulting compound several specific properties.

The chemical properties of sulpho-derivatives have been investigated in fair detail. Far less work has been done on the structure of the sulphonic acids and their derivatives, in particular on the way in which the SO_2R group interacts intramolecularly with the remainder of the molecule.

Much remains obscure in the structure of the sulpho-group itself, e.g. the character of the bonds formed by the sulphur atom, the part played by the d-orbitals of the sulphur atom in the formation of bonds, the stereochemistry of the sulpho-group, and the interaction between the sulpho-group and the rest of the molecule. There is as yet no generally accepted view on the type of electronic interaction occurring in the XSOY and XSO_2Y systems, where Y represents an organic radical and X = OH, OAlk, OAr, NR′R″, Hal, etc. Is conjugation present between the SO_2R group and the organic (in particular aromatic) radical or is this interaction different in character? Do the character and the intensity of this interaction change on passing to various derivatives of sulphonic acids? All the above questions have recently been attracting increasing attention from research workers. A study of the physicochemical properties of sulpho-compounds should obviously give an answer to these questions.

The present review covers work on the nature of sulphur–oxygen bonds and the infrared spectroscopy of oxygen compounds of sulphur.

II. GROUPS CONTAINING A SULPHUR–OXYGEN BOND

(a) Sulphur–Oxygen Bonds

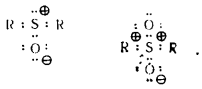
Organic compounds containing sulphur–oxygen bonds are classified as sulphoxides XSOY, sulphones XSO_2Y, sulphinic acids XSOOH, sulphonic acids XSO_2OH, and also various derivatives thereof (salts, halogeno- and amino-derivatives, esters, etc.). For a long time the nature of the sulphur–oxygen bond in these compounds was a subject of discussion, and this question cannot be regarded as finally settled even at the present time.

It can probably be supposed that the simple σ-bond between sulphur and oxygen is always supplemented by further interaction[1]. This additional bonding was shown by Cruickshank[2] to consist in interaction between the $2p$-orbital of oxygen and one of the $3d$-orbitals of the sulphur atom. In his view this interaction was universal, and could be considered as π-bonding.

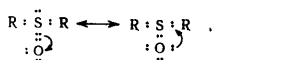
It was assumed[3-5] that the sulphur–oxygen bond was a covalent double bond. The valency of sulphur would then be 4 in sulphoxides, and 6 in sulphones. This would require that the octet rule must be assumed to break down, i.e. that sulphur will be surrounded by 10 electrons in a sulphoxide, and by 12 electrons in a sulphone:

Other authors[5-7] have attributed a polar coordinate single bond to these compounds. They assumed that oxygen

was bound to sulphur only by one pair of electrons, both of which had previously belonged to the sulphur:



It was supposed that complete loss of an electron by the sulphur atom occurred, i.e. that the bond became ionic in character. In other words, the sulphur–oxygen bond was interpreted as a covalent single bond plus an ionic bond, i.e. a so called "semipolar bond". This view was still used by Suter[8] in 1948 in discussing the dipole moments of diphenyl sulphones. Such a view still exists even now[9], with the reservation that the sulphur–oxygen bond is a resonance hybrid of two structures, but nevertheless the true state is closer to a semipolar double bond than to a covalent double bond:



In some experimental papers[4,10] such a concept of the sulphur–oxygen bonds is utilised to demonstrate the chemical properties of the compounds under investigation.

In several recent papers[11–16], however, doubt has been cast on the presence of a semipolar bond. This work has been based on exact measurements of parameters of the sulphinyl group (interatomic distances, bond angles, force constants, spectral data, and certain chemical properties). A summary table of bond lengths, bond orders, force constants, and bond angles has been given in a recent paper[15].

For various compounds the length of the sulphur–oxygen bond, measured by different methods[12,17,18], varies over the range 1.39–1.55 Å. This is shorter than the length of a simple covalent bond (1.70 Å) and in many compounds is shorter than a double bond (1.49 Å), all calculated from the covalent radii for sulphur–oxygen.

For most unionised oxygen compounds of sulphur–aliphatic and aromatic sulphoxides and sulphones, sulphonic acids and their esters, and also compounds such as the halogen derivatives of sulphurous and sulphuric acids—the length of the sulphur–oxygen bond is 1.42–1.47 Å (SO_2Cl_2 1.43,[9] SO_2 1.43,[12] $(CH_3)_2SO$ 1.47,[19] and SO_2F_2 1.405 Å[20,21]). This value increases sharply on passing to ions: thus for the ions $S_2O_6^{2-}$, $S_3O_6^{2-}$, SO_4^{2-}, and $S_2O_5^{2-}$ it varies from 1.46 ($S_2O_5^{2-}$) to 1.50 Å (for the remaining ions)[9,15,20–23]. For the ion HSO_4^- the length of the S–O(H) bond is given as 1.54 Å, and that of the S=O bond as 1.46 Å.[23–25] However, crystallographic measurements for the HSO_4^- ion in $NaHSO_4.H_2O$ gave corresponding values of S–O(H) 2.613 Å and S–O 1.450 Å.[26] The maximum sulphur–oxygen bond length of 1.66 Å has been found in the compound SF_5OOSF_5,[27] and 1.64 Å in SF_5OF.[28] The probable explanation of this is that, under the influence of five fluorine atoms, which interact vigorously with the 3*d*-orbitals of sulphur, the latter take practically no part in π-bonding with the 2*p*-orbitals of oxygen[29].

The shortest sulphur–oxygen bonds are found in the molecules SO_2F_2 (1.404 Å [21]) and SOF_2 (1.412 Å [30]). No attempts were made to explain this fact, but obviously no doubt attaches to the accuracy of these results, for it has subsequently been shown[15] that the shortest sulphur–oxygen distances correspond to the highest sulphur–oxygen stretching vibrations and force constants.

Cruickshank[2] considers that the sp^3d^2 state of sulphur is actually realised in the compound SO_2F_2, where the sulphur has six octahedral σ-orbitals, while the sulphur–oxygen bond is a true double bond. The same paper shows that the order of the sulphur–oxygen bonds always exceeds 1.50 for ions (SO_3^{2-} 1.50, $CH_3SO_3^-$ 1.58, FSO_3^- 1.67). This value increases considerably for unionised compounds (CH_3SO_2OH 1.81, CH_3SO_2F 1.88, CH_3OSO_2F 1.97), which is explained[2] by the lower electronegativity of the alkyl substituents.

Force constants of the sulphur–oxygen bond have been calculated[12,31,32] for several sulphones from the spectra. Subsequent investigations have shown poor agreement between these results and more recent calculations[15]. For example, Hungarian workers[12] obtained force constants of $(14.69–14.99) \times 10^{-5}$ dyn cm^{-1} for sulphones. However, Gillespie, Robinson, et al.[15,33–35] have obtained results giving considerably smaller values (in 10^{-5} dyn cm^{-1}—SO_4^{2-} 7.1, SO_3^{2-} 3.86, HSO_4^- 8.26, H_2SO_4 8.1, 10.29, $(CH_3)_2SO_2$ 9.48, SOF_2 10.95, SO_2F_2 12.05). Values given in several papers[2,9,12,15,36] for the O–S–O bond angle usually exceed the normal tetrahedral angle (109°). The lowest value (96°) is shown by the SO_3^{2-} ion. In other ions this parameter increases ($CH_3SO_3^-$ 106°, $ClSO_3^-$ 114°). In non-ionic compounds the angle approaches 120° and above (FSO_2OH 118°, CH_3OSO_2F 120°, CH_3SO_2F 122°, $(C_6H_5)_2SO_2$ 131°).

From a comparison of numerous experimental data on the lengths, orders, and force constants of sulphur–oxygen bonds, Gillespie and Robinson conclude[15] that a direct relationship exists between bond length and force constant: with increase in the sulphur–oxygen bond length the force constant decreases. The relationship can be expressed by the equation $\lg k_{SO} = -7.41 \lg r_{SO} + 7.15$.

A similar relationship exists between bond order and force constant: with increase in the multiplicity of the bond from 1.5 to 2.0 the force constant doubles.

A non-linear relation was obtained between bond order and bond length. It is not direct[2], but is represented by a curve recalling that for bond multiplicity as a function of bond length (for the carbon–carbon bond[20]).

According to Cruickshank and Robinson[24] the constants characterising the sulphur–oxygen bond are linked by the relations

$$k_{SO} \cdot r_{SO}^{7.4} = 1.41 \times 10^7$$

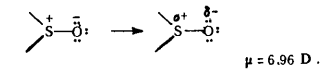
$$n_{SO} = 1.11 \times 10^{-6} \cdot k_{SO} + 0.7$$

$$r_{SO} = 1.70 - \frac{0.30}{1 + 0.46\left[\frac{2-n}{n-1}\right]}$$

$$r_{SO} = 1.69 - 0.40(n_{SO} - 1)$$

where k_{SO} is the force constant of the sulphur–oxygen bond, r_{SO} the interatomic sulphur–oxygen distance, $r_{SO}^{7.4}$ the corresponding distance for a force constant of 7.4, and n_{SO} the order of the sulphur–oxygen bond. Calculations based on these equations show satisfactory agreement with experimental values.

Calculation by means of the equation[9] for a semipolar double bond gives for the dipole moments of sulphur–oxygen bonds the value $\mu = 4.80 \times 1.45 = 6.96$ D (where 4.80×10^{-10} is the electrostatic charge on the electron, and 1.45 the experimental sulphur–oxygen distance in sulphones). This value (6.96 D) should correspond to the charge distribution



$\mu = 6.96$ D.

However, dipole moments of sulphur–oxygen bonds calculated from experimental data for certain sulphones[37] and also calculated by vector analysis[38] are considerably smaller (2.2–2.9 D), which probably indicates that a double bond is present between sulphur and oxygen.

The increase in dipole moments in the sequence

$CH_3SO_2CH_3$	$C_6H_5SO_2CH_3$	$C_6H_5SO_2C_6H_5$	p-$NH_2C_6H_4SO_2CH_3$
4.46D	4.73D	5.1D	6.09D

may constitute evidence that donor–acceptor interaction occurs between the sulphonyl group and the substituent, the sulphur acting as acceptor of electrons[13].

Several papers contain data on the dipole moments of various sulphonyl derivatives—sulphonic acids[39], sulphonyl chlorides[40,41], sulphinic acids[42].

Some workers conclude[2,9,15] that a simple σ-bond between sulphur and oxygen is supplemented by interaction between a $2p$-orbital of the oxygen atom and one of the $3d$-orbitals of the sulphur atom. This $2p-3d$ hybridisation, which is in general extremely weak, always develops, and can be regarded as π-bonding[43]. The bonding may be considerably strengthened if the electron affinity of the sulphur is increased by interaction with a strongly electronegative atom (e.g. fluorine), and also if the sulphur acquires a formal positive charge (as e.g. in a sulphonyl group). It is postulated also that the $3d$-orbitals undergo considerable compression in this type of interaction, which, of course, increases the energy of the bond.

In other words, the sulphur–oxygen bond can be regarded as in considerable measure a double bond with the electron cloud displaced towards the oxygen.

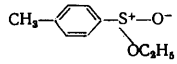
In view of the nature of the $3d$-orbitals, their overlapping with $2p$-orbitals of oxygen does not require exact agreement between the angles, as in $2p-2p$ bonding.

Similar conclusions are reached from molecular-orbital calculations of the molecules SO_2 and SO_3 and the ions SO_3^-, SO_3^{2-}, SO_4^{2-}, and $S_2O_3^{2-}$.[44,45]

(b) Geometry of the Groups XSOY, XSO_2Y, XSOOH, and XSO_2OH

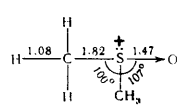
As has been shown above, it can now be regarded as proved that all cases of bond formation by sulphur involve its $3d$-orbitals. The contribution of d-orbital interaction may vary depending on the atom with which the sulphur is combined. If this atom is oxygen, the state of the sulphur atom will be s^2p^3d if surrounded by a decet of electrons, and sp^3d^2 if surrounded by a dodecet[46]. The first of these configurations corresponds to a pyramidal structure, and the second to an octahedral structure[20].

However, only one example—the sulphur hexafluoride molecule—is known of an octahedral configuration of sulphur. Such a configuration has not been found with the oxygen compounds of sulphur. Thus the study of sulphoxides, begun in 1925 by Phillips[47] on aromatic sulphoxides—ethyl toluene-p-sulphinate



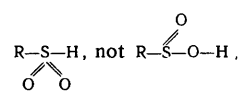
and then the work of Karrer et al.[48] showed the presence of optical isomerism in these compounds. Consequently sulphur in a sulphoxide must have a stable pyramidal structure, and may become a centre of asymmetry if all the substituents are different.

A crystallographic study of dimethyl sulphoxide[49] showed it actually to have a pyramidal structure, with the parameters



It may be supposed that in this case the nature of the bonds linking the sulphur atom will not influence the configuration. Actually, if all three bonds are semipolar σ-bonds, they will have a pyramidal p^3-distribution (the lone pair of electrons remaining in the $3s$-orbital of the sulphur[14]). If, however, the sulphur–oxygen bond is regarded as a covalent double π-bond, the bonds formed by $2p-3d$ interaction will also have a pyramidal arrangement, as Kucsman has shown[50].

Study of the vibrational spectra and of the dipole moments of sulphinic acids[42] led to the conclusion that they had the structure



In an SO_2H group sulphur is surrounded by four atoms, and the structure of the group is tetrahedral.

In sulphones, too, the structure of sulphur is close to a tetrahedron, but with considerable distortion of the bond angles. Thus for diphenyl sulphone Suter[8] gives 90° as the angle between the planes of the rings. Other workers[12,51] constructed a model of diphenyl sulphone by replacing one oxygen atom in an SO_3 group by two benzene rings, and found that one each of the two C–S and S=O bonds lies in the plane of one ring, and the other in that of the other ring. The planes of the rings are perpendicular, and the O–S–O angle is 120°. It is pointed out[12], however, that the angles may vary: for example, the O–S–O angle considerably exceeds the tetrahedral angle owing to the electrostatic repulsion between the oxygen atoms. It is assumed also that the C–S–C angle differs from 90°†. A recent work[9] gives the structure illustrated in Fig. 1 for bis-p-bromophenyl sulphone.

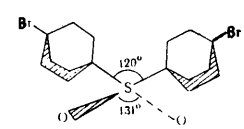
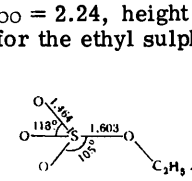


Figure 1. Diagram of molecule of bis-p-bromophenyl sulphone.

The sulpho-group in sulphonic acids and their derivatives has been assumed to have a tetrahedral structure[2,12,39,40,46,53]. However, the parameters of this pyramid are indicated only by Gur'yanova[40] for benzenesulphonyl chloride (interatomic distances), by Babaeva et al.[54] for the ion SO_3^- in Na_2SO_3 ($r_{SO} = 1.39$, $r_{OO} = 2.24$, height of pyramid 0.51 Å), and by Cruickshank[2] for the ethyl sulphate ion in potassium ethyl sulphate



Thus a tetrahedral structure, with the sulphur atom at the centre of the tetrahedron, is now generally accepted for the sulpho-group. With the polarity of the sulphur–oxygen bonds taken into account, such a structure for the

† More detailed information on the bond angles in these compounds will be found in Ref. 52.

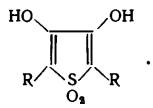
sulpho-group agrees well with the chemical properties[16], and also with the assignment of modes of vibration of sulphur–oxygen bonds in the Raman and infrared spectra[55].

(*c*) Nature of Interaction with Substituents

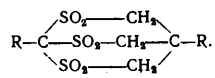
In view of the non-planar structure of the sulpho-group, it is apparently impossible to expect interaction involving conjugation of the sulpho-group with substituents. Nevertheless, it may be supposed that some interaction involving $2p-3d$ orbitals of the sulphur–oxygen bond may occur, provided that they are conveniently disposed in relation to unsaturated bonds of the substituents. There should also be some interaction of substituents transmitted through the sulphur atoms of the sulpho-group, without involving sulphur–oxygen bonds.

Both types of interaction actually occur. Thus Leandri et al.[14] showed, on the basis of the ultraviolet spectra over the range 200–300 nm for a large number of sulphoxides, that the sulphur atom is in this case in the $3sp^3$ state with one lone pair ($3s$). But besides this, weak conjugation is observed between this pair and the π-shell of unsaturated substituents. This interaction is responsible for extremely weak additional π-bonding in the sulphur–carbon(substituent) direction.

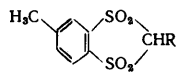
Moffitt showed[11,13] that conjugation along sulphur–oxygen bonds in sulphones is quite strongly developed when not prevented by the geometry of the molecule, e.g. in



This effect appears as a lowering of the sulphonyl frequencies in the infrared spectra and as a bathochromic shift of the bands in the ultraviolet spectra[56]. Such conjugation is also supported by results obtained by Doering[57–59], who studied the stabilising effect of the sulphonyl group on the carbanion derived from a bicyclic trisulphone of the type

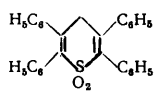


Koch and Moffitt[13] consider also that conjugation can occur in sulphones by means of a $2p$-orbital of a carbon atom (substituent), provided that these orbitals lie in the plane of the carbon–sulphur–carbon bonds. However, this is not consistent with results obtained by Jaffé[60] and Breslow[61], who studied pK_a values for the enolate ions of disulphonyl esters of the type

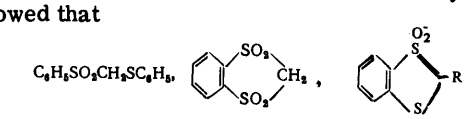


and showed that, owing to the geometrical structure of such compounds, when R = $COOC_2H_5$ [57–59] only conjugation of the type suggested by Moffitt[13] is possible. They established that there is no substantial conjugation between the $2p$-orbitals of the carbon atom and the hybrid orbitals of the sulphone.

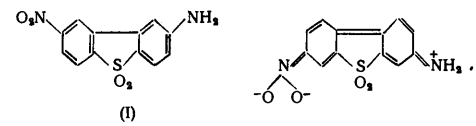
Suld and Price[62] synthesised compounds of the type



in which the "thiabenzene" ring was, in their opinion, conjugated (aromatic). This was not confirmed by Breslow[63], who showed that



have the same acidity, so that the anion is not stabilised by cyclic conjugation: i.e. it is not aromatic. Weak transmission of a conjugation effect through the sulphonyl group is suggested, even if the two rings are coplanar, by a comparison of the ultraviolet spectra of the two sulphones[9]



(I)

In compound (I) the effect of conjugation is transmitted through the sulphonyl group, whereas in the second compound it is transmitted away from this group. The ultraviolet spectrum of the second compound differs very greatly from those of (I) and of the unsubstituted sulphone.

Weak interaction of the sulphonyl group in alkyl phenyl and diphenyl sulphones is indicated also by other work[4,13,36,64–66], in which it was noted that interaction in *para*-substituted aromatic sulphones is strengthened by the introduction of electron-donor substituents. The explanation given was that the formal positive charge on the sulphur was responsible for certain of its electron-acceptor properties. The presence of a positive charge on the sulphur atom in dimethyl sulphoxide is suggested by recent spectroscopic results[67].

An assessment of the strength of interaction of the sulphonyl group from the Hammett σ-parameters[68] showed that this group possessed very little capacity for conjugation.

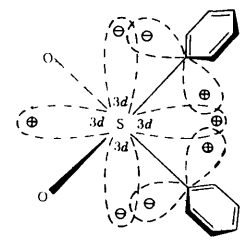


Figure 2. Scheme of electronic interaction due to $3d$-orbitals of the sulphur atom in diphenyl sulphone.

Assessing the possibility of interaction between the phenyl rings in diphenyl sulphone by means of the $3d$-orbitals of sulphur, i.e. without involving the sulphur–oxygen bonds, Price[9] points out that such interaction is quite real (Fig. 2); the two benzene rings may be non-coplanar[69]. As is evident from Fig. 2, the unsaturated orbitals of the two benzene rings—or more precisely the $2p$-orbitals of the carbon atoms—supply electrons to the free $3d$-orbitals of the sulphur, without involving the sulphur–oxygen bonds. The energy of such bonding will be slight.

In studies of the nature and strength of interaction by the sulpho-group in sulphonic acids[10,12] the authors write that "the sulpho-group (SO_2OH) does not interact with

strongly conjugated systems, such as, for example, benzene rings". This conclusion was reached from a study of the ultraviolet spectra of benzesulphonic acid. Comparison of the spectra of this acid with those of nitrobenzene, aniline, and benzoic acid showed that the SO_2OH group produces a far weaker bathochromic effect than do the nitro-, amino-, and carboxy-groups.

The vibrational structure of the absorption band is fairly well preserved in the ultraviolet spectra of substituted benzenesulphonic acids[10,64]. The authors consider that there is no conjugation between the sulpho-group and the ring, but that the sulphur exerts an electron-acceptor effect. This is demonstrated by the enhanced tendency to acylation of the amino-hydrogen atoms in the *p*-aminobenzenesulphonate ion. This occurs because the oxygen atoms of the sulpho-group in this ion carry a greater negative charge, while the positive charge on the sulphur diminishes. As a consequence, the sulphur shows less tendency to draw electrons out of the ring, which in turn weakens the displacement of the lone pair of electrons towards the ring.

To elucidate the character of the interaction between the SO_2R group and an aromatic system much information could be obtained by determining the substituent constants for the SO_2R group[70,71]. Exner[71] gives values of the induction constants σ_{ind} for a *p*-SO_2R group (SO_2O^- 0.25, SO_2NH_2 0.46, $SO_2OC_2H_5$ 0.63, SO_2Cl 0.86). It might be thought, however, that the induction constants do not reflect the actual character of the interaction, since the SO_2O^- and SO_2R groups (R = OAlk, NH_2, Hal) differ not only in the strength but also in the character of the interaction with the π-electron system of an aromatic radical.

From the above discussion it can obviously be assumed that interaction between a sulpho-group and a substituent is inductive and of electron-acceptor character rather than in the nature of conjugation. The strength of this interaction is comparatively slight. On passing to derivatives of sulphonic acids (chlorides, amides, esters) this interaction is considerably strengthened.

III. INFRARED SPECTRA OF OXYGEN COMPOUNDS OF SULPHUR

Study of the vibrational spectra of the oxygen compounds of sulphur was begun comparatively recently[18,72], at the end of the 1940s and the beginning of the 1950s. A considerable number of the papers known at the present time are still descriptive in character, and only during recent years have attempts been made to link the results of absorption spectroscopy with the structure and the properties of the oxygen compounds of sulphur. By no means all work undertaken with this aim was successful, obviously because the authors based their arguments on analogies with the carbonyl group[18]. These analogies (effect of substituents, participation in conjugation, effect of solvent) were unable, of course, to explain peculiarities observed in the infrared spectra of sulphinyl compounds, owing to the fundamental difference between these two groups both in symmetry and in electronic structure. It is now possible to link certain general features of the infrared spectra with the stereochemistry of the sulphinyl group, the nature of the substituent groups, the effect of the solvent, etc.

1. Appearance of Sulphur–Oxygen Bond in Infrared Spectra

Sulphur–oxygen bonds give strong bands in the infrared spectrum, the number of bands depending on the number of oxygen atoms attached to the sulphur. Thus the compounds XSOY give one band due to sulphur–oxygen stretching vibrations, while compounds of the type XSO_2Y give two bands. Furthermore, covalent compounds differ from ionised compounds in the position of the bands. In this way it is possible in principle to distinguish by means of the infrared spectrum the groups $\diagup$SO, $\diagdown$$SO_2$, and SO_3^-. This fact can be easily explained by considering the stereochemistry of the groups XSOY and XSO_2Y from the viewpoint of the possible vibrations of atoms in these groups. The stereochemistry of sulphur and the sulphonyl group has been discussed in the preceding Section. Here we consider only papers in which the authors discuss spatial structure directly from the viewpoint of possible modes of vibration.

The earlier work showed[18,72] that the infrared spectra of sulphoxides contain one strong band, which from its position could be assigned to a sulphur–oxygen stretching vibration (by analogy with sulphur monoxide[73]). It has since been shown[14,74] that the sulphoxide group has a quasi-tetrahedral structure with p^3d or sp^3d hybridisation. As is evident from Fig. 3, the site of one of the sulphur bonds is occupied by the orbital of the lone pair of electrons of the sulphur, and as a consequence the trigonal pyramid is extended to a tetrahedron. Such a structure, containing one oxygen atom, should, of course, have one sulphur–oxygen stretching vibration. O'Loane concluded[75] that the symmetry of the XSOY group should be *C*.

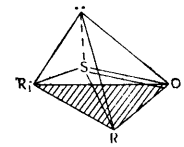


Figure 3. Structure of R_2SO group.

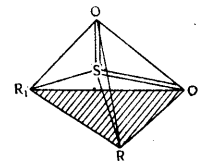
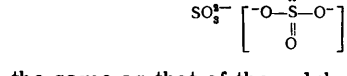
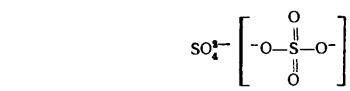


Figure 4. Structure of R_2SO_2 group

Discussion of the structure of the molecules XSO_2Y (see preceding Section) led to the conclusion that the sulphonyl group should be tetrahedral[74,76,77] (Fig. 4) or close thereto[78] both in covalent and in ionic compounds. According to Robinson[34] the spatial structure of the ion



will be the same as that of the sulphate ion



except that the position of one double bond is occupied in the sulphite ion by the lone pair of electrons of the sulphur. Consequently the modes of vibration of such ions will be identical.

These modes of vibration have been examined[79] with SO_2F_2 and the ion $CH_3OSO_2^-$ as examples[50]. The SO_2F_2 molecule has two planes of symmetry[80], one containing the two oxygen atoms, and the other the two fluorine atoms[77] (Fig. 5).

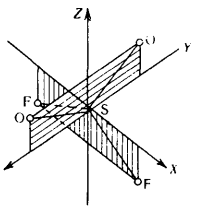


Figure 5. Diagram of SO_2F_2 molecule.

Assignment of all frequencies among types of vibrations has been made also for the simple molecules SO_3,[81] $SO_2(OH)_2$,[82,83] SO_2Cl_2,[78] and also SO_2F_2 and SO_2FCl.[84] An attempt to calculate the molecules SO_2Cl_2 and SO_2F_2 [77] was unsuccessful, for the frequencies calculated for the latter molecule did not agree with experiment. The symmetry of the group XSO_2Y is universally accepted as C_{2v},[79,80,82] and the sulphur–oxygen vibrations in such a molecule should comprise two stretching vibrations (symmetric and antisymmetric) and three deformation vibrations (twisting oscillations of sulphur–oxygen are forbidden in the infrared spectra[79]). In all a molecule having C_{2v} symmetry should describe nine normal vibrations[77], distributed among four types of symmetry:

$$C_{2v} = 4a(\nu_1; \nu_2; \nu_3; \nu_4) + a_2(\nu_5) + 2b_1(\nu_6; \nu_7) + 2b_2(\nu_8; \nu_9).$$

(*a*) Sulphur–oxygen stretching bands. Table 1[85] gives the sulphur–oxygen stretching frequencies in compounds of the type XSOY. The scatter in the results of different workers for each class of compounds does not exceed ±5 cm^{-1} from the value indicated in Table 1. It has been shown above that compounds XSO_2Y are characterised by bands due to antisymmetric and symmetric sulphur–oxygen stretching vibrations. Results for these compounds are listed in Table 2, set out in the same manner[85] as for the compounds XSOY. It is seen from Tables 1 and 2 that reliable experimental data are not available for all compounds, while certain classes of compounds have not been studied at all.

From a study of the effect of the immediate environment of an atom X in the groups $-X\overset{O}{\underset{O}{=}}$ on the X=O bonds Bellamy[86] concluded that, by analogy with carbonyl compounds[87], there should be a correlation here between the positions of the absorption bands due to the various bonds forming this group. Although it had been shown somewhat earlier, with nitro-compounds as example[88], that no satisfactory relation of such a kind is observed in these compounds, Bellamy[86] explained this by the presence of interaction between carbon–nitrogen stretching vibrations and ν_{NO_2} symmetric vibrations; furthermore, steric interactions are also possible between a substituent X and an oxygen atom in the nitro-group. Bellamy chose for investigation the compounds RSO_2R' (sulphones) and other compounds XSO_2Y (taken from Refs. 89–91). From these data a graph was plotted of the relative positions of the sulphur–oxygen stretching bands. Fig. 6 shows that the bands due to antisymmetric and symmetric sulphur–oxygen vibrations are arranged in two fairly clustered groups. The slight scatter in the values may be caused by the fact that not all the substances were examined under identical conditions, most of them being in solution, but several in the vapour state.

Table 1. Position of bands due to sulphur–oxygen stretching vibrations in compounds of the type XSOY.

X	Y						
	O–	>C	Cl	OH	OAlk	OC_6H_5	F
>C	1020	1050	1150	1090	1130		
Cl	980	1150	1231		1213		
OAlk		1130	1213		1200		
OC_6H_5						1245	
F							1312

Table 2. Position of bands due to sulphur–oxygen stretching vibrations in compounds of the type XSO_2Y.

X	Y							
	O–	>C	SR	Cl	N	OH	OR	F
C_g^u	1190 1050	1325 1140	1340 1150	1380 1170	1350 1165	1350 1160	1365 1176	1400 1200
Cl		1380 1170		1437 1205				
OR	1200 1050	1365 1175					1400 1200	
CF_3	1270 1030	1360 1120	1422 1235	1439 1239	1380 1200			1475 1240
F		1400 1200						1502 1269

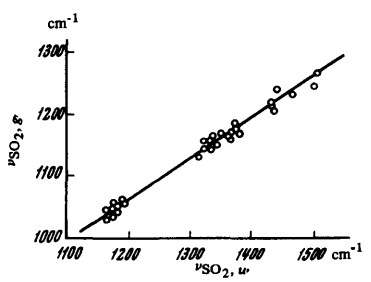


Figure 6. Relative positions of absorption bands due to symmetric and antisymmetric sulphur–oxygen stretching vibrations.

Somewhat later Robinson showed[92] that the positions of $\nu_{SO_2,g}$ and $\nu_{SO_2,u}$ are fully consistent with this relationship in other compounds of the type XSO_2Y, the ions XSO_3^- and SO_4^{2-}, and also in those cases in which the sulphonyl group is located in a ring or a chain. This correlation proved

to be very useful, since, if the position of one band in the infrared spectrum is known, the other can be found without difficulty. For this purpose the formula $\nu_u = 1.470$, $\nu_g = 359$ was proposed[86].

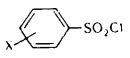
It has since proved possible to work either with the position of only one band[93] or with the half-sum of the bands $\frac{1}{2}(\nu_u + \nu_g)$‡, since this quantity is practically constant for all compounds[27,94]. The constancy of this parameter probably indicates that there is no or only very weak interaction between the sulphur–oxygen bonds in the compounds XSO_2Y.[15]

No systematic investigation was made into the shape or width of the sulphur–oxygen stretching bands. There are merely indications that these bands are usually symmetrical[95,96]. The band due to antisymmetric sulphur–oxygen stretching vibrations in compounds XSO_2Y is almost always broad and is often split into several maxima[97,98]. The band due to symmetric vibrations appears as a single peak (except in the case of $RSO_2NR'R''$ [99]), which is very convenient for the determination of intensities[100].

(*b*) Sulphur–oxygen deformation vibrations. Information on other modes of vibration of sulphur–oxygen bonds is still more scanty than that on the stretching vibrations, and is often less reliable. No systematic searches for these vibrations have been made. As has been shown above, among nine normal vibrations in a molecule X_2SO_2 there should be four deformation vibrations involving the sulphur–oxygen bonds—ν_3 (A_1) scissor, ν_7 (B_1) rocking, ν_9 (B_2) rocking, and ν_5 (A_2) twisting.

Table 3 shows that the majority of compounds investigated are various sulphonyl chlorides; there are far fewer representatives of sulphonic acids and their derivatives or of ions. The frequency ranges are 500–600 cm^{-1} for acid halides, 775–900 cm^{-1} for sulphonic acids and their esters, and 530–670 cm^{-1} for various ions. It is not yet possible to draw any definite conclusions from available data, either on the exact value of δ_{SO} nor, still less, on the influence of various factors on them.

Table 3. Position of bands due to deformation vibrations δ_{SO}.

Compound	Frequency, cm^{-1}	Mode of vibration	Ref.
SOF_4	481	wagging	
	640	wagging	
SO_2Cl_2	586	scissors	80
SO_2F_2	544	deformation	84
	539	rocking	
SO_2FCl	480	deformation	84
	505	rocking	
$SO_2(OH)_2$	563	deformation	84
	563	rocking	
CH_3SO_2OH	480	wagging	101*
	501	rocking	
	534	scissors	
$SO_2(OH)Cl$	482	deformation	84
	513	rocking	
$SO_2(OH)F$	556	wagging	101*
	545	or scissors	
	568	rocking	
	556		
SO_2	519	deformation	
CH_3SO_2Cl	528	ditto	76
CH_3SO_2F	534	»	
$ArSO_2OH$	860	»	102
$C_6H_5SO_2OC_2H_5$	900	»	98
$CH_3C_6H_4SO_2OC_2H_5$	788	»	98
$TolylSO_2OC_2H_5$	778	»	98
$AlkSO_2Cl$	565	»	103
	590	scissors	
	545	rocking	
	532—570	rocking	97**
	565—610	scissors	
	570	deformation	104
$AlkSO_2O^-$	620	deformation	
	530	antisymmetric	
$AlkSO_2O^-$		deformation	
	590	symmetric	104
SO_3^{2-}	615—660	deformation	105
		ditto	
SO_4^{2-}	580—670	»	
HSO_4^-	570—600	»	
		deformation	
SO_3^{2-}	494	symmetric	
	632	deformation	54
$(NH_4)_2SO_4$	616—655	symmetric	106
		deformation	

* Small differences in frequency are observed with liquid and gaseous specimens.

** For compounds of the type $R(SO_2Cl)_2$ the authors indicate that the bands are split into two.

(*c*) Other bands in the spectra of compounds XSOY and XSO_2Y. Published information on the presence of other vibrations involving sulphur–oxygen bonds in the infrared spectra of oxygen compounds of sulphur is extremely scanty, and it all relates to sulphonyl chlorides. Thus for benzenesulphonyl chloride a band has been found at 800 cm^{-1} and assigned to vibrations of the S–OR group[103]. Bands at 407 or 413 cm^{-1} [78] in the $HOSO_2$. .Cl molecule and a band at 412 cm^{-1} in the $HOSO_2OH$ molecule[107] are assigned[107] to the S–OH group.

With compounds XSO_2Y a band of moderate intensity is often observed in the region of 1100 cm^{-1}. The assignment of this band is still a matter for discussion. This band in the ion SO_4^{2-} in aqueous solution and in the solid state (at 1104 and 1108 cm^{-1} respectively) is attributed by Herzberg[73] to one of the main skeletal vibrations of the tetrahedron. In sulphates $MSO_4.nH_2O$ it is located at 1105–1090 cm^{-1}.[108,109]

This band is almost always present in covalent compounds. It has frequencies of 1063–1072 cm^{-1} in propanesulphonic acid and its anhydride[110]. In sulphinic acids Detoni and Hadzi[102] found it at 1000 cm^{-1} and ascribed it to sulphur–oxygen oscillations in the appropriate structures. Their results indicate that this band is more intense in the esters than in the acids themselves. The weakening of intensity and some lowering of its frequency in the free acids are explained by intermolecular hydrogen bonding.

Study of aromatic sulphonyl chlorides showed[76,98,103] the presence of a band of moderate intensity in the range 1095–1099 cm^{-1}. It was regarded as characteristic of an aromatic chlorosulphonyl group ($ArSO_2Cl$). It has been suggested[91,111] that this band may belong either to sulphur–nitrogen vibrations in sulphonamides§ or to the first overtone of sulphonyl deformation vibrations, and it may also be due to planar carbon–hydrogen deformation vibrations.

Detoni and Hadzi[98] showed that a band always appeared at 1060–1100 cm^{-1} in a large number of compounds comprising sulphonic acids (other than ethanesulphonic acid), their esters, chlorides, and amides. This band was therefore regarded as the first overtone of an O–SO deformation vibration, analogous to the overtone of OSO in SO_2Cl.[80]

Bellamy[115], who detected this band in diphenyl sulphoxide at 1096 cm^{-1}, studied its displacements under the influence of the solvent. He assigned this band to vibrations of a phenyl ring, and explained its displacement on passing to polar solvents by the presence of Fermi resonance.

‡ This was first suggested in 1949.[18]

§ In some investigations of the infrared spectra of aromatic sulphonyl chlorides, however, this band was not observed [112,113]. Tosilini[114] assigned the frequency 829–910 cm^{-1} in compounds $RSO_2N:CH.R'$ to vibration of the sulphur–nitrogen bond.

Some part of the polar character of the sulphur–oxygen bonds is then transferred to absorption by an aromatic ring. This is supported by the fact that, in a strongly polar solvent, where the sulphur–oxygen bands undergo the greatest shifts, the intensity of the 1096 cm^{-1} band drops sharply.

Thus it is evidently still premature to draw final conclusions on the assignment of the 1100 cm^{-1} band.

2. Factors affecting Position of Sulphur–Oxygen Stretching Bands

The geometry of the groups enclosing the sulphur–oxygen bonds is of decisive importance among the various factors influencing the position of bands due to stretching vibrations of these bonds. As has been shown above, the stereochemistry of sulphur in various valency states leads to a tetrahedral or nearly tetrahedral structure for both XSOY and XSO_2Y compounds. It can therefore be assumed that the influence of both substituents and other factors on the position of these stretching bands is explained by the same causes in both classes of compounds. We shall therefore discuss all the information on the various factors for the two classes of compounds together. However, it is useful to consider covalent compounds separately from ionic compounds, since the sulphur–oxygen frequencies in the latter are far less sensitive to the various factors.

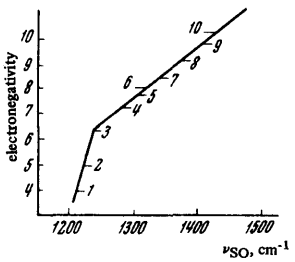


Figure 7. Correlation of electronegativity of substituents with position of sulphur–oxygen stretching bands in compounds R_2SO and R_2SO_2:
1) $(RO)_2SO$; *2*) ROSOCl; *3*) $SOCl_2$; *4*) $(RO)_2SO_2$; *5*) RSO_2OR; *6*) SOF_2; *7*) RSO_2; *8*) RSO_2Cl; *9*) SO_2Cl_2; *10*) RSO_2F.

A. Covalent Compounds

A systematic study of the influence of substituents on the position of sulphur–oxygen stretching bands must probably be regarded as starting with a paper by Bellamy and Williams[86]. On the basis of a few published data[90] and their own experimental work they showed that symmetric and antisymmetric vibrations of sulphur–oxygen bonds in compounds RSO_2R' depend on the nature of the substituent groups.

Below we shall examine the position of sulphur–oxygen stretching bands as a function of various constants of the substituents X and Y, and also the effect of the solvent.

(*a*) Effect of substituents

Electronegativity of substituents. A relation between the position of the ν_{SO_2} frequencies and the electronegativity of the substituents was first shown by Szmant and Emerson[93]. Their results (Fig. 7) indicate that the frequencies of the sulphur–oxygen bonds increase with increase in the electronegativity of the substituent Y in compounds CH_3SOY and CH_3SO_2Y (for compounds containing a sulphonyl group they plotted the antisymmetric bands along the horizontal axis, and the effective electronegativity according to Kagaraise's data[116] along the vertical axis). It is seen from Fig. 7 that the sulphonyl group is far more sensitive to variation in the electronegativity of the substituent than is the sulphoxide group $\diagdown S{-}O \diagup$.

Robinson[92] showed that, in a large number of compounds, increase in the electronegativity of the substituents is accompanied by a shift in the antisymmetric and symmetric sulphur–oxygen bands to higher frequencies (Table 4).

Table 4. Position of ν_{SO_2} bands in compounds XSO_2Y.

Group	Type of compounds	ν_{SO_2}, cm^{-1}	
		symmetric	antisymmetric
C—SO_2—F	sulphonyl fluorides	1203—1210	1401—1412
C—SO_2—Cl	sulphonyl chlorides	1169—1185	1365—1390
C—SO_2—O	sulphonic acids and esters	1165—1185	1360—1375
C—SO_2—N	sulphonamides	1152—1169	1336—1358
C—SO_2—S	thiosulphonates	1144—1154	1331—1342
C—SO_2—C	sulphones	1136—1160	1307—1334
O—SO_2—F; F—SO_2—F etc. HSO_3F		1230—1260	1445—1510
O—SO_2—Cl; $HOSO_2Cl$ etc. $S_2O_5Cl_2$		1205—1225	1408—1452
O—SO_2—O	covalent sulphates	1137—1195	1390—1415
N—SO_2—N	sulphamides	1163	1350

Thus a linear relation exists between these two parameters, the rise in the frequency ν_{SO} corresponding exactly with the increase in the electronegativity of the substituent:

$$F > OF > CF_3 > OR \simeq OH > Cl \simeq \simeq CCl_3 > SR \simeq NH_2 > Ar > R.$$

This sequence reproduces in essentials Pauling's electronegativity series[117]. The highest value of sulphur–oxygen stretching vibrations has probably been found[118] for the compound SF_5OOSF_5.

Aliphatic, aromatic, and conjugated substituents X and Y. The replacement of aliphatic by aromatic substituents in sulphoxides produces a considerable drop in the frequency ν_{SO} in non-polar solvents[96] (cm^{-1}):

CH_3SOCH_3	1069
$C_6H_5CH_2SOCH_2C_6H_5$	1056
$C_6H_5SOCH_2C_6H_5$	1054
$C_6H_5SOCH_3$	1055
$C_6H_5SOC_6H_5$	1052

Contrary to the views of Bellamy[85], the compounds XSO_2Y exhibit several differences in the position of absorption frequencies between diaryl and dialkyl sulphones. This is readily noticeable in the spectra of sulphones, but is far less readily seen in the spectra of other compounds[119] (Table 5). From Table 5 it is seen that, if the sulphonyl group is linked with two alkyl radicals, the symmetric frequencies ν_{SO_2} lie in the range 1136–1145 cm^{-1}, while in the diaryl or alkyl aryl derivatives this band has been displaced to the range 1150–1160 cm^{-1}. The antisymmetric stretching band is less sensitive, lying in both cases in the range 1312–1334 cm^{-1}.

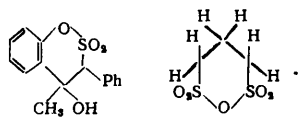
Conjugated substituents somewhat lower the frequencies of both bands (Table 5), although not always; in the compounds $RSO_2N{:}CH.R'$ the frequencies of the sulphonyl group remained practically constant whatever the substituents R and R'.

A study[93] of the cyclic sulphites $[C]_n$ $S{=}O$ showed that the position of the bands was almost independent of whether the ring contained five, six, or seven carbon atoms.

Table 5. Effect of nature of substituent on position of ν_{SO_2} bands.

Compounds	ν_{SO_2}, cm^{-1}		Ref.
	symmetric	antisymmetric	
Sulphones			
Ethyl methyl sulphone	1145	1330	72
Methyl phenyl sulphone	1160	1334	18
Diphenyl sulphone	1158	1319	120
Methyl vinyl sulphone	1139	1312	121
Allyl methyl sulphone	1136	1307	121
Sulphonic esters			
$R{-}SO_2{-}OR'$			
Methyl ethanesulphonate	1165	1356	122
Methyl toluene-*p*-sulphonate	1185	1375	72
Phenyl toluene-*p*-sulphonate	1170	1375	123
Sulphonamides			
$R{-}SO_2{-}NH_2$			
Methanesulphonamide	1169	1336	123
Benzenesulphonamide	1167	1358	72
Sulphonyl chlorides			
$R{-}SO_2{-}Cl$			
Methanesulphonyl chloride	1175	1370	76
Benzenesulphonyl chloride	1185	1390	72

Later work has shown that the position of sulphur–oxygen stretching bands is independent of the size of the ring also in the compounds[124,110]



The infrared spectra of alkane-1-sulphonates from C_1 to C_{13} indicated no dependence of the frequency ν_{SO_2} on the length of the carbon chain. Thus the symmetric sulphur–oxygen stretching vibrations were found to be located at 1060, 1055, 1062, and 1063 cm^{-1} for C_1, C_3, C_6, and C_{12}, etc.[125]

In a study of the effect of degree of substitution at the nitrogen atom in the sulphonamide group[114] on the ν_{SO_2} frequencies it was shown that in *N*-alkylated sulphonamides the sulphur–oxygen frequencies are practically constant—ν_g = 1150–1170 cm^{-1} and ν_u = 1310–1350 cm^{-1}—and only in a quaternary sulphonamide group do they rise to 1180 and 1388 cm^{-1} respectively.

In sulphoxide complexes having the composition $[[(CH_3)_2.SO]_2M][MX_4]$ the ν_{SO} frequency was found[114] to be ~ 1000 cm^{-1} independently of the metal.

In the compounds $ArSO_2CR{:}CR'R''$ the band due to the sulphonyl group has been found[126] to depend neither on *cis–trans* isomerism nor on the nature of R, R', or R''.

The infrared spectra of twenty-seven thiosulphones $RSSO_2R'$ have been examined[127]. The properties of the sulphonyl group are unaffected by the substituent: the position of the ν_{SO_2} bands is affected neither by the nature of the radical SR nor by steric hindrance in *ortho*-substituted SAr substituents. The position of the bands due to symmetric and antisymmetric SO_2-stretching vibrations in thiosulphones $RSSO_2R'$ is analogous to that in the corresponding sulphones RSO_2R'.

An attempt has recently been made to express quantitatively the effect of substituents on the position of sulphur–oxygen stretching vibrations[94]. The formula used was

$$\frac{1}{2}(\nu_g + \nu_u) = \nu^0 + x_i \cdot x_j$$

where ν^0 = 907 cm^{-1} is a universal constant and x_i and x_j are empirical constants characterising individual substituents attached to the sulphonyl group, which were determined graphically (Fig. 8). This graph was plotted from published data, and the calculated values of x_i and x_j are given in Table 6.

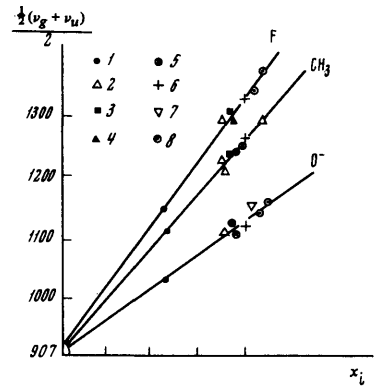


Figure 8. Explanation in text:
1) O^-; *2*) R; *3*) C_6H_5; *4*) NH_2; *5*) OR; *6*) Cl; *7*) CF_3; *8*) F.

Table 6. Values of the constants x_i and x_j for various substituents.

Substituent	x	Substituent	x
F	21.7	C_6H_5, $CH_3C_6H_4$ (*o*, *m*, *p*)	18.5
CF_3	21	Sulphonic esters	18.2
Cl	20.1	cyclo-C_6H_{11}	17.8
OR (Alk)	19.7	$-CH{=}CH_2$	17.8
OH	19.5	$-CH_2CH{=}CH_2$	17.7
NH_2	19.0	O^-	11.4

Exner combined his equation with Bellamy's equation[86], and obtained two equations from which it was possible to calculate values of ν_g and ν_u for vibrations of SO_2: ν_g = 880 + 0.810x_ix_j and ν_u = 934 + 1.190x_ix_j, the empirical constants x in these equations being given in Table 6. He considers that these empirical constants represent mainly the inductive effect of the substituents, and that adequate confirmation of this is provided by the linear relation between the Taft σ-parameter and the values of x for various substituents (Fig. 9).

Exner asserts that the quantity ν^0 = 907 cm^{-1} has a physical meaning, although the nature of this meaning is not yet known. A somewhat unexpected conclusion is that the effect of substituents on the characteristic sulphur–oxygen stretching frequencies is non-additive. Robinson's data

(Table 4 in Ref. 92) indicate strict additivity in the effect of substituents on the frequencies:

$$\begin{array}{lll} \text{C—SO}_2\text{—C} & 1136\ \text{cm}^{-1} & \\ \text{C—SO}_2\text{—F} & 1203\ \text{cm}^{-1} & \Delta\nu = 67\ \text{cm}^{-1} \\ \text{C—SO}_2\text{—O} & 1165\ \text{cm}^{-1} & \Delta\nu = 30\ \text{cm}^{-1} \\ & & \Sigma\Delta\nu = 97\ \text{cm}^{-1} \\ \text{O—SO}_2\text{—F} & 1230\ \text{cm}^{-1} & (\Delta\nu = 94\ \text{cm}^{-1}) \end{array}.$$

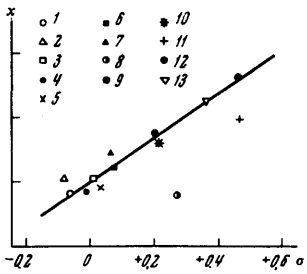


Figure 9. Explanation in text:
1) C_6H_{11}; *2*) R; *3*) $CH_2C_6H_5$; *4*) $CH_2{:}CHCH_2$; *5*) $CH_2{:}CH$; *6*) C_6H_5; *7*) NH_2; *8*) C_6H_5S; *9*) OR; *10*) OH; *11*) Cl; *12*) F; *13*) CF_3.

Table 7. Effect of solvent on the frequency ν_{SO} in dimethyl sulphoxide.

Solvent	ν_{SO}	Solvent	ν_{SO}
Cyclohexane	1083	1,2-Dichloroethane	1061
Tetrachloroethylene	1074	Dibromoethane	1061
Carbon disulphide	1070	Acetonitrile	1058
Carbon tetrachloride	1069	Nitromethane	1057
Benzene	1068	Dichloromethane	1057
Acetone	1064	Methyl chloride	1054
		Di-iodomethane	1051

(*b*) Solvent effect

The influence of solvents on the position of the ν_{SO_2} bands has been studied systematically only for the simple triatomic molecules COS and SO_2.[128] The positions of the absorption bands due to symmetric and antisymmetric stretching vibrations of sulphur dioxide have been examined in fifteen aliphatic and ten aromatic solvents. For $\nu_{SO_2,g}$ the smallest shifts (relative to the gas phase) have been found for solutions in n-hexane and in nitrobenzene (~ 6 cm^{-1}), and the largest shifts in di-iodomethane and in mesitylene (~ 11 cm^{-1}). For $\nu_{SO_2,u}$ the smallest shifts occur in n-hexane (~ 14.5 cm^{-1}) and in fluorobenzene (21 cm^{-1}), and the largest in acetone (28.5 cm^{-1}) and in mesitylene (29.5 cm^{-1}). It was established that in any solvent the shifts in the symmetric bands were always much smaller than those in the antisymmetric bands.

Relatively few data are available for more complicated compounds. As shown by Barnard et al.[18] and also by subsequent work[95,115,126,129,130], sulphoxides exhibit some displacement of the ν_{SO} band to lower frequencies in polar solvents (nitromethane) and in those capable of forming hydrogen bonds (alcohols, chloroform). This is evident in the case of dimethyl sulphoxide[27] (Table 7).

Biscarini[95] has shown that the equilibrium

$$R'R''SO + HX \rightleftarrows R'R''SO \ldots HX$$

is established in solutions of a sulphoxide in a mixture of a polar and a non-polar solvent. The compounds XSO_2Y have not been systematically studied from this point of view. The few results scattered in different papers provide no basis for generalisations: it can only be said that the ν_{SO_2} bands are displaced very slightly to lower frequencies in proton-donor solvents.

Thus the frequencies of sulphur–oxygen stretching vibrations in covalent compounds undergo substantial shifts only under the influence of change in the electronegativity of the substituents. For sulphoxides

$$\begin{array}{ll} \text{C—SO—C} & 1050\ \text{cm}^{-1} \\ \text{F—SO—F} & 1312\ \text{cm}^{-1} \end{array}$$

for sulphones, sulphonic acids, and their derivatives

$$\begin{array}{ll} \text{C—SO}_2\text{—C} & 1140\ \text{cm}^{-1} \\ & 1325\ \text{cm}^{-1} \\ \text{F—SO}_2\text{—F} & 1269\ \text{cm}^{-1} \\ & 1502\ \text{cm}^{-1} \end{array}.$$

All other factors produce far smaller displacements of the bands.

It must also be noted that the "sensitivity" of sulphonyl compounds is about half that of their carbonyl analogues[93]:

$$\begin{array}{lll} F_2CO & 1928\ \text{cm}^{-1} & \Delta\nu_{CO} = 219\ \text{cm}^{-1} \\ (RO)_2CO & 1709\ \text{cm}^{-1} & \\ F_2SO & 1312\ \text{cm}^{-1} & \\ (RO)_2SO & 1202\ \text{cm}^{-1} & \Delta\nu_{SO} = 110\ \text{cm}^{-1} \end{array}.$$

B. Ionic Compounds

Ionised compounds are characterised by a marked lowering of the sulphur–oxygen stretching frequencies: $\nu_{SO_2,g}$ = 986–1082 cm^{-1} and $\nu_{SO_2,u}$ = 1090–1218 cm^{-1}.[92] Organic and inorganic sulphites and sulphates, both in solution and in the solid state, lie within these ranges. Such a drop in frequency is usually explained by a decrease in the "double-bondedness" of the sulphur–oxygen bond. The ion $X{-}SO_2{-}O^-$ is assumed to have a tetrahedral structure[34,54,104,106,108,109,131] of symmetry C_{3v}. There are indications that the tetrahedron is not regular[108].

The influence of various factors (primarily the nature of the substituent) on the sulphur–oxygen vibrational frequency is considerably less marked in ions than in covalent compounds. Thus Haszeldine pointed out[89] that the introduction of fluorine into the anion RSO_2O^- has no effect on the position of the band due to symmetric sulphur–oxygen vibrations, while the bands due to antisymmetric vibrations are slightly raised.

Robinson has shown[92] that increasing the electronegativity of the substituent X in the ion XSO_3^- raises the symmetric bands but has no effect on the antisymmetric bands: ν_{SO_2} = 1040, 1054, 1080 cm^{-1} for HSO_4^-, $ClSO_3^-$, FSO_3^-.

Gamo[108], Ross[109], and Nakamoto[132] have shown that the bands due to stretching vibrations in crystalline hydrates of metal sulphates and in metal complexes containing the sulpho-group ($-SO_2OH$) lie in the ranges $\nu_{SO_2,g}$ = 1100–1090 cm^{-1} (doublet) and $\nu_{SO_2,u}$ = 1140–1145 cm^{-1}, being independent both of the metal in the salts and on the composition of the complex.

Ionised organic sulphonates were studied in the form of the cyclohexylamine salts by la Lau and Dahmen[104]. These workers showed that the symmetric and antisymmetric ν_{SO_2} bands lie at 1040–1050 and 1180 cm^{-1} respectively. It was found that the position of the bands did not depend on the

nature of the radical. The antisymmetric band is usually broad, and is often split into several maxima.

With regard to other regions of the infrared spectrum, Miller[105] showed that there were several bands which could be assigned to an ionised sulpho-group: SO_3^{2-} sulphite at 615–660 cm^{-1}, SO_4^{2-} sulphate at 580–670 cm^{-1}, and HSO_4^- hydrogen sulphate at 570–600 cm^{-1}. Although recent papers have been specially devoted to the infrared spectra of sulphuric acid[82,83,133–135], the assignment of bands in these spectra encounters great difficulties, primarily owing to the fact that sulphuric acid and its aqueous solutions are strongly associated. Furthermore, the spectrum of H_3O^+ (the oxonium cation) is superimposed on that of sulphuric acid itself, which also greatly increases the difficulty of assignment.

Conversion of a covalent into an ionic compound substantially lowers the frequencies of stretching vibrations[136]. This indicates that a large negative charge is delocalised on the oxygen atoms and that the sulphur–oxygen bonds are lengthened, becoming at the same time more "single" and simple. The proportion of 3*d*-orbital interaction with the sulphur atom correspondingly diminishes, and transmission of a substituent effect to the sulphur–oxygen bond in the ion is hindered.

3. Relation between Sulphur–Oxygen Stretching Frequencies and Parameters of the Sulphur–Oxygen Bond

The correlation of parameters characterising the sulphur–oxygen bond with the frequencies of sulphur–oxygen stretching vibrations forms the subject of a single paper by Gillespie and Robinson[15], in which practically all the known experimental information is assembled.

(*a*) Bond lengths and angles. These workers found a definite link (Fig. 10) between the sulphur–oxygen bond lengths determined by various methods, both for covalent and for ionic compounds, and the position of the bands due to sulphur–oxygen stretching vibrations. They regard this relation as universal, and it can be used to predict such bond lengths in molecules where direct measurement is not possible. The accuracy of a prediction is ±0.02 Å.

It has been shown also that a linear correlation exists between the O–S–O bond angles and the sulphur–oxygen stretching frequencies (Fig. 11). Gillespie and Robinson showed further that these angles can be evaluated from the equation $\nu_{SO_2,g}/\nu_{SO_2,u} = \frac{1}{2}(1 + \cos^2\alpha)/(1 + \sin^2\alpha)$, if the frequencies are known. Values showing good agreement with experiment are obtained both by calculation and by interpolation (Fig. 8).

(*b*) Force constants of sulphur–oxygen bond. Gillespie and Robinson assume that there is no interaction between the sulphur–oxygen vibrations in the $\diagdown SO_2$ group, as also with other vibrations in the molecule¶. Then the force constant can be deduced from a consideration of the sulphonyl group as a simple triatomic molecule:

$$k_{SO} = \frac{5.889 \cdot \nu_{SO_2} \cdot 10^{-2}}{\left(\frac{1}{m_S} + \frac{1}{m_O}\right)} = 0.6282\,\nu_{SO_2},$$

where m_S and m_O are the atomic weights of sulphur and oxygen. Values of k_{SO} calculated by means of this equation agree well with results obtained by other methods. These workers obtain the same relationship between the frequency ν_{SO} and the bond order as between this frequency and the bond length, since a linear relationship exists between the order and the length of a bond.

¶ However, this is not always true[115].

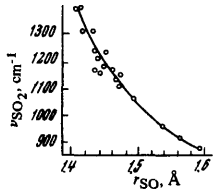


Figure 10. Correlation between position of absorption bands due to sulphur–oxygen stretching vibrations and bond length.

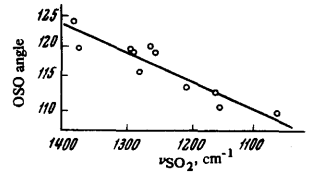


Figure 11. Correlation between sulphur–oxygen stretching frequencies and O–S–O bond angles.

Table 8. Correlation between $\nu_{SO_2,g}$ and acidity constant of sulphonic acid in sulphuric acid.

Acid	$\nu_{SO_2,g}$, cm^{-1}	K_a (25°C), mole kg^{-1}
Disulphuric	1240	0.014
Fluorosulphuric	1230	0.002
Chlorosulphuric	1209	0.001
Sulphuric	1195	—
Benzenesulphonic	1182	base
Toluene-*p*-sulphonic	1170	base

(*c*) Dissociation constants of sulphonic acids. The ν_{SO_2} vibration frequencies have been compared with the strength of the corresponding sulphonic acid, as measured by the dissociation constant of this acid in sulphuric acid[92].

It was shown that the larger is the value of K_a, the higher the frequency of the symmetric stretching vibration (Table 8). Thus the strength sequence of the various sulphonic acids relative to sulphuric acid was assessed from the SO_2-stretching frequencies to be

$$H_2S_2O_7 > FSO_3H > CF_3SO_3H > ClSO_3H < H_2SO_4 < CH_3SO_3H.$$

4. Intensity of ν_{SO_2} Bands

Very little work has been published on the intensities of the ν_{SO_2} bands. In 1961 Ghersetti[96] measured the intensity of ν_{SO} for five sulphoxides, and showed that it depended on the solvent, but did not explain this fact (Table 9). In a

non-polar solvent (carbon tetrachloride) dimethyl sulphoxide forms intermolecular dimers[67], as is shown by the changes in intensity of the 1060-cm^{-1} band. On passing to polar solvents dimethyl sulphoxide showed an increase in intensity ($10^{-4}A$), from cyclohexane 1.62 to carbon tetrachloride 1.87 and acetonitrile 1.90.

Table 9. Intensity of ν_{SO} band in some sulphoxides (dissolved in carbon tetrachloride).

Sulphoxide	ν_{SO}	$10^{-2}\epsilon^a$	$\Delta\nu_{1/2}$	$10^{-4}A$
Dimethyl	1069	7.7	15.5	1.87
Dibenzyl	1056	7.0	14.0	1.60
Benzyl phenyl	1054	8.2	10.2	1.26
Methyl phenyl	1055	7.1	9.5	1.01
Diphenyl	1052	7.8	9.0	1.00

Table 10. Intensity of $\nu_{SO_2, g}$ band in some sulphones.

Sulphone	$10^{-4}A$
Dibutyl	$1.38 \cdot 10^{-4}$
Methyl vinyl	$1.57 \cdot 10^{-4}$
Methyl phenyl	$2.1 \cdot 10^{-4}$
m-Methoxyphenyl methyl	$2.1 \cdot 10^{-4}$
p-Methoxyphenyl methyl	$3.1 \cdot 10^{-4}$

Table 11. Intensity of ν_{SO_2} stretching bands in compounds XSO_2Y.

Compounds	Stretching vibration	$10^{-2}B$	Standard deviation *s*
Sulphones	ν_{SO_2}, *g*	64.5	20.4
C—SO_2—C	ν_{SO_2}, *u*	66.5	10.7
Sulphonamides	ν_{SO_2}, *g*	91.3	18.4
C—SO_2—N	ν_{SO_2}, *u*	92.0	18.0
Sulphonic acids	ν_{SO_2}	238	50.5
C—SO_2—O	ν_{SO_2}	46.0	14.6

Five sulphones were examined by Rogers[137], who showed that the integral intensity of the ν_{SO_2} bands increases on passing to conjugated substituents (Table 10). The integral intensity of the symmetric SO_2-stretching bands can be correlated with the Taft constants (σ_{ind} and σ_R) for various sulphones[138].

Flett[100] has investigated a far larger number of compounds (Table 11). According to his results the bands are usually more intense in aromatic than in aliphatic compounds.

An attempt has been made[139] to determine sulpho-compounds quantitatively by means of the intensities of the ν_{SO_2} bands.

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Hydroxyalkylphosphines and Hydroxyalkylphosphine Oxides

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The paper discusses the condensation of phosphine and of primary and secondary phosphines with aliphatic and aromatic aldehydes and ketones, the reaction mechanisms, and the influence of the structure of the starting materials on the final products.
A detailed account is given of the chemical properties of the hydroxymethylphosphonium halides and of hydroxymethylphosphines and -phosphine oxides. Particular attention is paid to the reactions of tervalent phosphorus—oxidation, addition of sulphur, formation of quaternary phosphonium compounds with alkyl halides, alkene oxides, aldehydes, unsaturated acids, and other compounds—and also reactions at the labile hydrogen atom of the hydroxymethyl groups in hydroxymethylphosphines.
Information is given on methods for preparing organophosphorus polymers from tetrakishydroxymethylphosphonium chloride and its derivatives by the processes of polytransesterification, alcoholysis, phenolysis, and polycondensation with nitrogen-containing compounds. Problems of the practical application of the products are examined. The bibliography contains 162 references.

CONTENTS

I. Introduction 532
II. Condensation of phosphine and of primary and secondary phosphines with aldehydes and ketones 532
III. Chemical properties of hydroxymethylphosphonium halides and of hydroxymethyl-phosphines and -phosphine oxides 537
IV. Preparation of phosphorus-containing polymers based on tetrakishydroxymethylphosphonium chloride and its derivatives 539

I. INTRODUCTION

An important place in the chemistry of organophosphorus compounds is occupied by compounds containing a coordinatively unsaturated phosphorus atom. Among them are phosphites and phosphines, by means of which it is possible to synthesise diverse derivatives containing tervalent and quinquevalent phosphorus. The Michaelis and Arbuzov reactions, which have served as foundation for numerous researches on the chemistry of organic phosphorus compounds, are based on the use of acid and normal phosphites.

The present paper gives information, widely scattered in the literature, on the condensation of phosphine and of primary and secondary phosphines with aldehydes and ketones, the chemical properties of the condensation products, and the use of hydroxymethylphosphonium halides and of hydroxymethyl-phosphines and -phosphine oxides for the synthesis of organophosphorus polymers possessing flame-resistant and ion-exchange properties, and of alkylenediphosphine oxides suitable for use as extractants in the recovery and preparation of valuable elements.

II. CONDENSATION OF PHOSPHINE AND OF PRIMARY AND SECONDARY PHOSPHINES WITH ALDEHYDES AND KETONES

Hoffmann was the first to show that phosphine reacts with formaldehyde in the presence of hydrochloric acid at 80°C in the absence of stirring with the slow formation of tetrakishydroxymethylphosphonium chloride[1,2]:

$$PH_3 + 4CH_2O + HCl \rightarrow [P(CH_2OH)_4]^+\bar{Cl}.$$

It has since been established that the reaction is best conducted with a molar ratio of formaldehyde to hydrochloric acid of 4.2 : 1 at 20°C with vigorous stirring. These conditions ensure good absorption of phosphine and its reaction with formaldehyde. The yield of tetrakishydroxymethylphosphonium chloride reaches 85–90%.[3-7]

Condensation between phosphine and formaldehyde takes place not only under the influence of acids but also in the presence of many metals of Groups II–VII or their salts, as well as in the absence of catalysts. Good results are given by the use of mercury, silver, platinum, or palladium deposited on kieselguhr or pumice[7-9]. The reaction

is usually conducted in aqueous–alcoholic and aqueous dioxan solutions at temperatures between −10° and +40°C. When phosphine is passed into aqueous formaldehyde (pH 4–8), tetrakishydroxymethylphosphonium hydroxide $(HOCH_2)_4POH$ (pH 8.5) is formed initially[8–10], and is then further treated with phosphine, without being isolated, to be converted into trishydroxymethylphosphine (pH 6.5).[9,11] This last compound is obtained also from paraformaldehyde, suspended in water or acetonitrile, and phosphine in the presence of platinum(IV) chloride at 20–35°C:[9]

$$PH_3 + CH_2O \xrightarrow{PtCl_4\ etc.} \begin{matrix} P(CH_2OH)_3 \\ [P(CH_2OH)_4]^+\,\bar{O}H \end{matrix}.$$

Interaction between phosphine and aqueous formaldehyde under a pressure of 150–300 mmHg at 40–80°C gives a good yield of tetrakishydroxymethylphosphonium hydroxide[12,13]. When paraformaldehyde is used, the reaction is conducted at 40 atm and 80–100°C in the absence of solvent or catalyst, when a high yield of trishydroxymethylphosphine is obtained[14–16].

The hydroxymethylation of phosphine can be accomplished also in the absence of pressure, by passing phosphine into heated paraformaldehyde. Under these conditions, however, the yield of trishydroxymethylphosphine is considerably diminished[17].

Tetrakishydroxymethylphosphonium chloride consists of colourless crystals of m.p. 151°C,[17] soluble in water and the lower aliphatic alcohols but insoluble in most of the usual organic solvents. Aqueous solutions of tetrakishydroxymethylphosphonium chloride have a strongly acid reaction: at 20°C a 10% solution has pH 1.92. On neutralisation to pH not exceeding 6.5 the solutions are stable on storage for a long time[18].

Tetrakishydroxymethylphosphonium hydroxide is a colourless viscous oil, sparingly soluble in water, the pH of the solution being 8.5. With an alcoholic solution of mercuric chloride it forms the complex $(HOCH_2)_4POH.HgCl_2$ melting at 140°C, which is insoluble in water and alcohol[8,10].

Trishydroxymethylphosphine is a colourless substance of m.p. 58°C, which boils with decomposition at 115°C (2.5 mmHg [13]), and possesses the characteristic odour of phosphines. It is readily soluble in water and alcohol, but does not dissolve in non-polar organic solvents. It forms yellow adducts with quinol $(HOCH_2)_3P.C_6H_4O_2$ (m.p. 160°C) and a complex with mercuric chloride $(HOCH_2)_3P.HgCl_2$ (m.p. 135°C). Unlike the simple phosphines, which possess weakly basic properties, trishydroxymethylphosphine has a slightly acid reaction in water (pH 6.5).[9,15] Trishydroxymethylphosphine can be used as intermediate in the synthesis of various organophosphorus compounds and also of insecticides, as a component of flame-resistant treatments for textiles and wood, and as an additive to lubricating oils.

In some cases phosphines reacts with other aldehydes, depending on their structure, in the same way as with formaldehyde, to form tetrakishydroxyalkylphosphonium salts, whereas in other cases more complicated compounds are formed. The peculiarity of these reactions is mostly due to transformations of unstable intermediate products of the condensation of one or two aldehyde molecules with the phosphine.

Aldehydes without branching at the α-carbon atom react similarly to formaldehyde with phosphine. It was initially supposed that, in the presence of hydrogen chloride and bromide in ether, adducts are formed containing four moles of the aldehyde together with one mole each of phosphine and the hydrogen halide, which were not isolated in pure form[19]:

$$4\,RC\begin{matrix}O\\H\end{matrix} + PH_3 \xrightarrow{HCl} \left(R{-}C\begin{matrix}O\\H\end{matrix}\right)_4 \cdot PH_3 \cdot HCl.$$

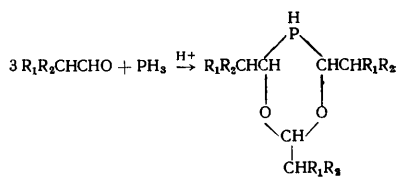
When the reaction was conducted in the presence of aqueous mineral acids (hydrochloric, hydrobromic, hydriodic, sulphuric, orthophosphoric, nitric), substances were isolated in pure form which proved to be tetrakis-1-hydroxylalkylphosphonium salts[20–23]:

$$4\,RC\begin{matrix}O\\H\end{matrix} + PH_3 \xrightarrow{HCl} \left[P\left(\begin{matrix}CH{-}R\\|\\OH\end{matrix}\right)_4\right]^+\bar{C}l$$

where R = C_{1-18} alkyl.

Good results are obtained if the aldehyde is slowly added to the reaction mixture, and organic solvents (tetrahydrofuran, butanol, dioxan) are used to increase the solubility of the phosphine and the higher aldehydes. Negative results are obtained when the reaction is conducted in the gas phase in the presence of a catalyst (aluminium silicate) at 375°C; at higher temperatures the phosphine decomposes to white phosphorus and hydrogen[20].

Aldehydes which are branched at the α-position react readily with phosphine in the presence of hydrochloric acid at room temperature, but unlike the unbranched aldehydes they form cyclic secondary phosphines having a six-membered ring. This reaction has been studied with isobutyraldehyde and 2-ethylhexanal as examples. The former gave a 75% yield of 2,4,6-tri-isopropyl-1,3-dioxa-5-phosphacyclohexane (I), and the latter a 90% yield of 2,4,6-tris-1′-ethylpentyl-1,3-dioxa-5-phosphacyclohexane (II):[20,24]



where (I) $R_1 = R_2 = CH_3$ and (II) $R_1 = C_2H_5$, $R_2 = n\text{-}C_4H_9$.

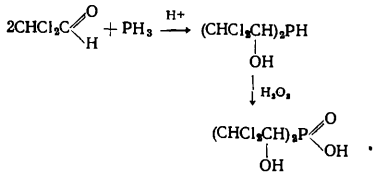
The compound (I) reacts with sulphur in benzene to form the corresponding sulphide, which possesses herbicidal activity[25]. It is assumed that the reaction involves the intermediate formation of secondary phosphines $[R_1R_2CHCH(OH)]_2PH$, which are unable to form quaternary phosphonium salts because of steric hindrance, but react with the aldehyde to give six-membered cyclic phosphines. The products have been subjected to detailed study.

Chlorinated aldehydes also react with phosphine. Chloroacetaldehyde and phosphine in the presence of hydrochloric acid (ratio 3 : 1) form an amorphous solid, which could not be isolated in pure form[20]. In the presence of a catalyst (platinum tetrachloride) it is assumed that tris-2-chloro-1-hydroxyethylphosphine is produced[26]:

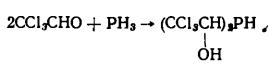
$$ClCH_2CHO + PH_3 \xrightarrow{PtCl_4} P\left(\begin{matrix}CH{-}CH_2Cl\\|\\OH\end{matrix}\right)_3.$$

Phosphine reacts with dichloroacetaldehyde in the presence of concentrated hydrochloric acid in tetrahydrofuran with the assumed formation of bis-2,2-dichloro-1-hydroxyethylphosphine, which also could not be isolated as an

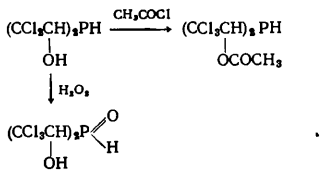
individual compound. On oxidation this product is converted into bis-2,2-dichloro-1-hydroxyethylphosphinic acid[20]:



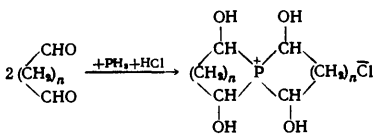
In contrast to the mono- and di-halogenated aldehydes, chloral and chloral hydrate react very vigorously with phosphine to give a 95% yield of bis-2,2,2-trichloro-1-hydroxyethylphosphine[20,27-29]:



Tris-2,2,2-trichloro-1-hydroxyethylphosphine was also obtained in this reaction[30]. On oxidation with hydrogen peroxide it yields the corresponding phosphine oxide, and on acetylation a diacetyl derivative[20]:

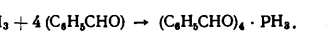


Dialdehydes, among which glutaraldehyde and succinaldehyde have been studied as examples, react readily with phosphine in the presence of concentrated hydrochloric acid in tetrahydrofuran at 20°C.[20] The products of this reaction are relatively stable five- and six-membered spirocyclic phosphonium salts. Glutaraldehyde gives a 65% yield of 2,2',6,6'-tetrahydroxy-1,1'-spirobiphosphanium chloride (I), and succinaldehyde a 34% yield of 2,2',5,5'-tetrahydroxy-1,1'-spirobiphospholanium chloride (II):

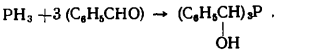


where (I) $n = 3$ and (II) $n = 2$. These spirans and their nitrogen analogues are difficultly accessible compounds.

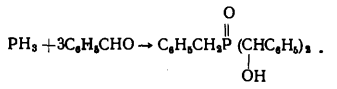
It was originally considered that phosphine reacts with aromatic aldehydes in roughly the same way as with aliphatic aldehydes. It was supposed that the interaction of benzaldehyde and phosphine in the presence of hydrogen chloride in ethereal solution gave a crystalline adduct[19]:



This has since been assigned the structure of tris-α-hydroxybenzylphosphine[31]:

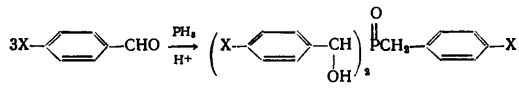


However, the compound was then found to be benzylbis-1-hydroxybenzylphosphine oxide†, whose formation involves the transfer of oxygen from carbon to phosphorus[33,35]:



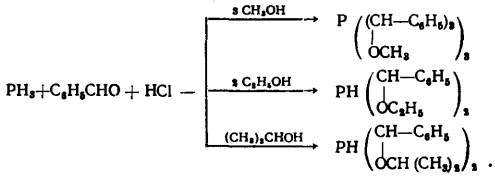
The structure of the product as an oxide is supported by many data[32,33].

Substituted aromatic aldehydes react similarly to benzaldehyde with phosphine in dioxan or tetrahydrofuran[33,35]:



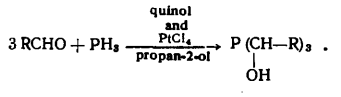
where X = Cl, Br, CH_3, C_3H_7. *p*-Nitrobenzaldehyde, *p*-hydroxybenzaldehyde, and naphthaldehyde also react with phosphine, but it has not proved possible to isolate the reaction products in pure form and establish their structure.

Benzaldehyde reacts differently with phosphine in alcoholic solution, different products being formed according to the alcohol taken[31]—tris-α-methoxybenzylphosphine in methanol, bis-α-ethoxybenzylphosphine in ethanol, and bis-α-isopropoxybenzylphosphine in propan-2-ol:



It is assumed that hemiacetals are formed in the first stage of this reaction, and these react with phosphine by a bimolecular or a termolecular mechanism[36].

Various aldehydes are able to react with phosphine in the presence of catalysts other than mineral acids to form tertiary α-hydroxy-phosphines[26], e.g.

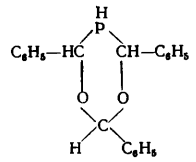


The compounds obtained, like trishydroxymethylphosphine, can be used as intermediates for organic synthesis, as insecticides, and as additives for lubricating oils.

The first attempts to promote reaction between phosphine and ketones in the presence of catalytic quantities of an acid were unsuccessful[37]. However, it has since been found that this reaction goes readily in strongly acid media.

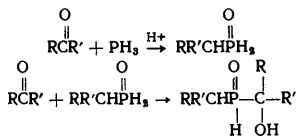
A mixture of two products—a primary phosphine oxide and a secondary 1-hydroxyalkylphosphine oxide—is obtained by the interaction of phosphine and a ketone (mixed with concentrated hydrochloric acid) in the molar proportions 1:3. Formation of the first of these products involves the transfer of oxygen from the carbonyl carbon to

† The cyclic acetal



is formed in 10–40% yield as a by-product[31,34].

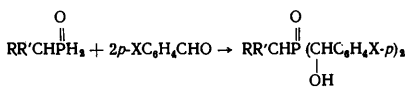
phosphorus, while the second involves the normal carbonyl addition of the ketone to the primary phosphine oxide[38,39]:



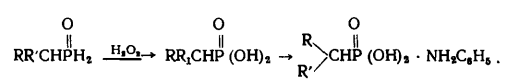
where R and R′ = alkyl, aryl.

The reaction was accomplished by passing phosphine into a solution of the ketone in concentrated hydrochloric acid at room temperature. The proportions of the products formed depends on the nature of the ketones, which can be arranged in the sequence—cyclohexanone < cyclopentanone < acetone < pentan-2-one < heptan-2-one < < pentan-3-one < acetophenone < heptan-4-one—according to increasing quantity of the primary phosphine oxide formed. The ratio of this primary product to the secondary phosphine oxide varies correspondingly from 9 : 1 with heptan-4-one to 1 : 9 with cyclohexanone, and the duration of the reaction from 30 min with cyclohexanone to 11 h with heptan-4-one; acetophenone reacts at the same rate as acetone[37].

Primary phosphine oxides, which are stable in acid solution at −80°C, have not been isolated in individual form. The presence of such compounds in the reaction mixture was proved by converting them into various derivatives. Thus treatment with aromatic aldehydes gave the corresponding tertiary bishydroxyalkylphosphine oxides:

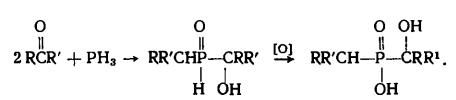


where X = H, Cl; and on oxidation the phosphonic acids were isolated (as their aniline salts):

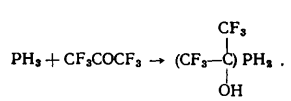


Thus the condensation of phosphines with ketones provides a convenient method for obtaining alkylphosphonic acids in which the phosphorus is bound to a secondary carbon atom.

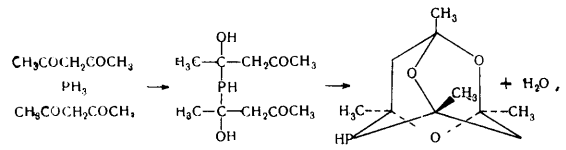
Secondary hydroxyalkylphosphine oxides have been isolated as crystalline substances from the reactions of cyclohexanone, cyclopentanone, acetone, and acetophenone with phosphine. On oxidation with nitric acid or hydrogen peroxide they gave the corresponding phosphinic acids:



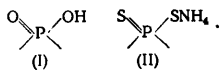
Hexafluoroacetone reacts with phosphine when heated in an autoclave to form as the sole product 2,2,2-trifluoro-1-hydroxy-1-trifluoromethylethylphosphine[40,41]:



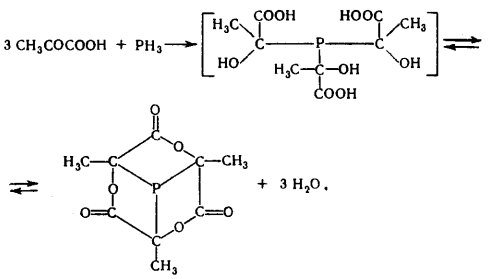
Diketones also react readily with phosphine, but heterocyclic systems are formed[42]. For example, the reaction with pentane-2,4-dione in hydrochloric acid solution has been studied, and crystalline 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphadamantane isolated, obviously formed via an intermediate secondary phosphine:



The chemical properties of the product were typical of secondary phosphines. Oxidation with hydrogen peroxide gave the phosphinic acid (I), and treatment with sulphur and ammonium hydroxide yielded the ammonium phosphinodithioate (II)



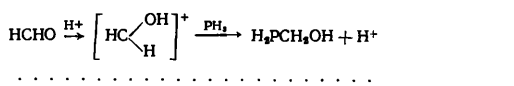
In the presence of ethereal hydrogen chloride phosphine reacts also with pyruvic acid (in the molar proportions 1 : 3) to give an almost quantitative yield of a compound $C_9H_9O_6P$, presumably with intramolecular esterification of carboxyl and hydroxyl groups present in an intermediate unstable tertiary phosphine[33]:



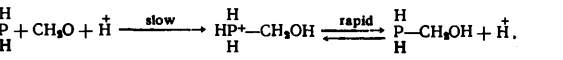
Thus the structure of the product represents a tricyclic system, in which three five-membered rings have fused at the phosphorus atom. The most intense absorption bands in the infrared spectrum of this compound are located near 1784 cm^{-1}, which corresponds to stretching vibrations of an ester carbonyl group, while no absorption bands are present corresponding to stretching vibrations of COOH and OH groups. The above reaction is general in character, and has been studied in a series of other acids of formula RCOCOOH, where R = C_{1-6} alkyl[43].

The reactions of phosphine with aldehydes and ketones yield various products depending on the starting materials, the catalysts, and the solvents. However, it is generally accepted that, whatever the final products, these reactions are very similar in their mechanism in the early stages of condensation with phosphine. Several opinions, sometimes differing only in details, are held concerning the mechanism of this reaction. According to one of them the interaction of phosphine with formaldehyde catalysed by a proton involves the initial formation of a "formaldehyde cation", which then reacts with more phosphine to give hydroxymethylphosphine and a proton. The latter again enters into reaction with formaldehyde to form the formaldehyde cation, which reacts with the hydroxymethylphosphine to give bis- and tris-hydroxymethylphosphines, and

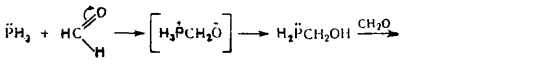
ultimately tetrakishydroxymethylphosphonium salts or bases[44]:



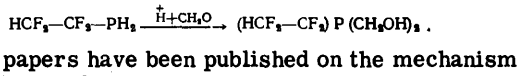
Besides this bimolecular mechanism, a termolecular reaction mechanism has been suggested, involving the initial formation of a monohydroxyalkylphosphonium salt, which is converted into a monohydroxyalkylphosphine with loss of a proton, and then into di- and tri-substituted phosphines and phosphonium salts or bases:



When condensation takes place in the absence of a catalyst, it is assumed that an intermediate phosphine—formaldehyde complex is formed, which is converted into hydroxymethylphosphine and then, by an analogous scheme, reacts with formaldehyde to form bis- and tris-hydroxymethylphosphines and tetrakishydroxymethylphosphonium hydroxide[13,15]:

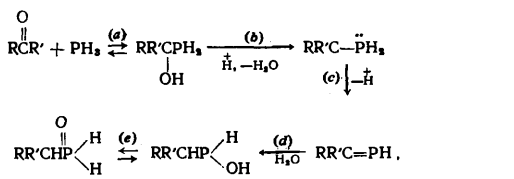


The ability of phosphine and of methyl- and dimethylphosphines to add formaldehyde is governed by the nucleophilic character of the former and the polarity of the C=O bond in the latter. The reactivity of the phosphines varies in conformity with their nucleophilic character[15] in the sequence $PH_3 < CH_3PH_2 < (CH_3)_2PH$, and when it is very low[45-49] phosphines do not react with formaldehyde in the absence of a catalyst. For example, 1,1,2,2-tetrafluoroethylphosphine, which possesses weak electron-donor power, yields with formaldehyde bishydroxymethyltetrafluoroethylphosphine only in the presence of hydrochloric acid[13]:



Several papers have been published on the mechanism of the reactions undergone by phosphine and alkylphosphines with formaldehyde; studies have been made of the kinetics, and the activation energies have been calculated[50].

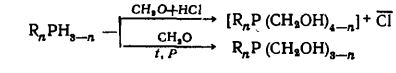
For phosphine the mechanism of the reaction, accompanied by the transfer of oxygen from carbon to phosphorus, is expressed by the scheme[37]



Phosphine first adds to the ketone as to aliphatic aldehydes (*a*). In strongly acid medium a carbonium ion is formed [*b*], which is stabilised as an intermediate compound containing a carbon–phosphorus double bond (*c*), hydration of which (*d*) yields a primary phosphine oxide (*e*).

Data have been published indicating that reactions involving the migration of oxygen from phosphorus to carbon are analogous to allyl rearrangements, and represent a general phenomenon for the series of α-substituted derivatives of tervalent phosphorus[51].

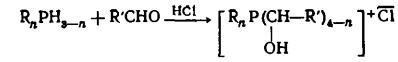
Like phosphine itself, primary and secondary phosphines react with aqueous formaldehyde in the presence of an equimolecular quantity of hydrochloric acid to form quaternary phosphonium salts[37,52-56], but when heated (to 65–100°C) with paraformaldehyde under pressure hydroxymethylphosphines are formed[13,52,57-61]:



where $n = 1, 2$ and R = alkyl, aryl.

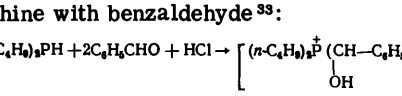
Hydroxymethylphosphonium salts are more stable towards hydrolysis[52] than are quaternary alkylhydroxymethylammonium salts, which are decomposed by water to amine hydrochlorides and formaldehyde.

The condensation of primary and secondary phosphines with aldehydes and ketones is greatly influenced by the structure of both components. Study of the reactions of aliphatic aldehydes with phosphines (propyl-, phenyl-, and diphenyl-phosphines) has shown that, in the presence of an equimolecular quantity of hydrochloric acid, phosphonium chlorides are formed[33,37,55,62,63]:

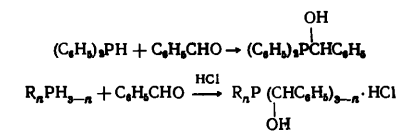


where $n = 1, 2$, R = alkyl, aryl, and R′ = alkyl.

A quaternary phosphonium salt is formed also by dibutylphosphine with benzaldehyde[33]:

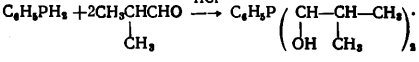


In the presence of traces of hydrochloric acid benzaldehyde condenses with diphenyl-, dicyclohexyl-, and isobutylphosphines to give tertiary phosphines[37,55,64,65] or their hydrochlorides[37]:

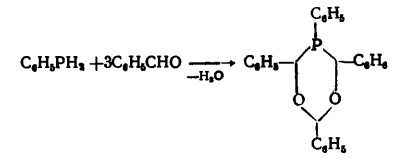


where $n = 1, 2$ and R = iso-C_4H_9, cyclo-C_6H_{11}.

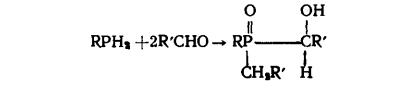
Phenylphosphine forms with isobutyraldehyde the hydrochloride of a tertiary phosphine even in excess of hydrochloric acid at 20°C:[37]



With benzaldehyde in the presence of a small amount of hydrogen chloride in acetonitrile or methanol phenylphosphine gives a 59% yield of a cyclic product[37]:



In boiling strongly acid medium primary phosphines react with aromatic aldehydes, and secondary phosphines (diphenylphosphine) react with aliphatic and aromatic aldehydes, to form phosphine oxides[37]:

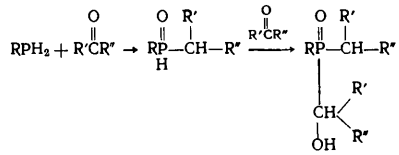


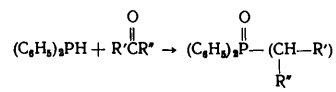
where R = alkyl, cycloalkyl, aryl and R′ = aryl, naphthyl;

$$(C_6H_5)_2PH + RCHO \rightarrow (C_6H_5)_2PCH_2R \quad (O)$$

where R = alkyl, aryl, naphthyl.

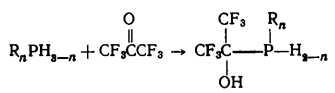
Primary and secondary aromatic phosphines react with ketones in strongly acid medium on heating to form the corresponding tertiary phosphine oxides‡ [37]:





where R = alkyl, aryl, cycloalkyl, and R′, R″ = alkyl, aryl or R′ + R″ = cycloalkyl, indol-1-yl.

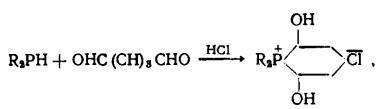
Fluorinated ketones form with primary and secondary phosphines the corresponding 1-hydroxyalkylphosphines [40,41]:



where n = 1, 2 and R = CH_3.

Several primary phosphines (isobutyl-, octyl-, phenylphosphines), on treatment with pentane-2,4-dione, give crystalline polycyclic tertiary phosphines [42].

A cyclic phosphonium salt is obtained from a dialdehyde and a secondary phosphine [66]:



Thus the reactions undergone by phosphine and phosphines with aldehydes and ketones can be divided into two groups—reactions involving normal carbonyl addition with formation of phosphines, their salts, and quaternary phosphonium bases, and reactions accompanied by migration of oxygen from carbon to phosphorus in the hydroxymethylphosphines produced initially, and leading to the synthesis of tertiary phosphine oxides.

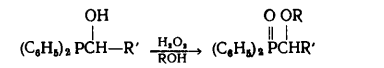
III. CHEMICAL PROPERTIES OF HYDROXYMETHYLPHOSPHONIUM HALIDES AND OF HYDROXYMETHYLPHOSPHINES AND -PHOSPHINE OXIDES

Trishydroxymethylphosphine and substituted hydroxymethylphosphines, like other compounds containing a tervalent phosphorus atom, are readily oxidised, and sulphur, and form quaternary phosphonium compounds: i.e. the chemical properties of hydroxymethylphosphines, like those of other phosphines, are determined by the presence of a coordinatively unsaturated phosphorus atom. Thus on oxidation with oxygen [52,64,67], hydrogen peroxide [13,15,37,68-71], nitric acid [67], peracetic acid [52], potassium permanganate [67], and oxides of nitrogen they are converted into phosphine oxides§.

$$R_nP(CH_2OH)_{3-n} \xrightarrow{1/2\,O_2} R_nP(O)(CH_2OH)_{3-n}$$

where n = 0–2 and R = alkyl, aryl, fluorinated alkyl, cycloalkyl.

Oxidation in alcohol yields α-alkoxyalkylphosphine oxides [37]:



where R = alkyl, aryl and R′ = naphthyl.

With sulphur trishydroxymethylphosphine and substituted hydroxymethylphosphines form phosphine sulphides [52,72,73]:

$$R_nP(CH_2OH)_{3-n} \xrightarrow{S} R_nP(S)(CH_2OH)_{3-n}$$

where n = 0–2 and R = alkyl, aryl.

Trishydroxymethylphosphine and substituted hydroxymethylphosphines react with alkyl halides and with toluene-p-sulphonic and alkyl- and aryl-phosphonic esters to form quaternary phosphonium salts [16,17,56,63,74-78]:

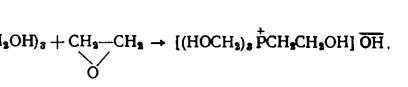
$$R_nP(CH_2OH)_{3-n} \xrightarrow{R'X} [R_nR'P(CH_2OH)_{3-n}]^+\overline{X}$$

where n = 0–2, R = alkyl, aryl, and X = halogen, anion of corresponding acid.

Trishydroxymethylphosphine is readily alkylated even in the course of formation. Thus the interaction of phosphine with formaldehyde in the presence of a catalyst (a salt of a metal in Groups II–VII) and an alkylating agent yields an alkyl(aryl)trishydroxymethylphosphonium halide [79-81]:

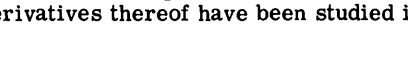
$$PH_3 + CH_2O + RX \rightarrow [RP(CH_2OH)_3]^+\overline{X}.$$

Trishydroxymethylphosphine and dialkyl(aryl)hydroxymethylphosphines react with dihalogenoalkanes, both in solution and in the absence of a solvent, to give a quantitative yield of the quaternary phosphonium salts [75,82]:

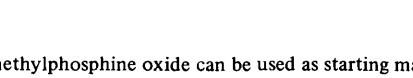


where n = 1–4, m = 0–2, R = alkyl, aryl, and X = Br, I.

Quaternary phosphonium compounds are obtained also by the interaction of trishydroxymethylphosphine with alkylene oxides [83-85] at 50–100°C in water or in an organic solvent which is miscible with water (dimethylformamide, acetonitrile, lower alcohols, ketones). Quaternary phosphonium salts are obtained in the presence of mineral or organic acids, and quaternary phosphonium hydroxides in their absence:



Quaternary phosphonium bases and salts are formed by the action of aldehydes on trishydroxymethylphosphine in the presence of water, a mineral acid, or an organic acid. Saturated and unsaturated aliphatic and aromatic aldehydes and various derivatives thereof have been studied in this reaction [10]:



Trishydroxymethylphosphine reacts with hydroxymethylated derivatives of urea to form quaternary phosphonium

‡ In the case of primary phosphines the reaction involves the addition of one or two molecules of the ketone depending on the structure of the initial phosphine and the ketone.

§ Trishydroxymethylphosphine oxide can be used as starting material for various syntheses and in flame-resistant treatments for textiles and wood.

compounds, which are recommended as intermediates in the production of flame-resistant fibre-forming plastics[86]:

$$P(CH_2OH)_3 \xrightarrow{NH_2CONH(CH_2OH)} [P(CH_2OH)_3CH_2NHCONH_2]^+\overline{OH}.$$

The action on trishydroxymethylphosphine of $\alpha\beta$-unsaturated aliphatic acids, their esters, and their amides in the presence of water and acids in a water-soluble organic solvent yields phosphorus analogues of betaines[87]:

$$P(CH_2OH)_3 \xrightarrow{CH_2=CHCOOH} \begin{matrix} \overset{+}{P}(CH_2OH)_3 \\ | \\ CH_2CH_2COO \end{matrix}.$$

Treatment of trishydroxymethylphosphine with $\alpha\beta$-unsaturated nitriles produces unstable phosphonium salts, which are able to split off hydroxymethyl groups. Thus with three moles of acrylonitrile trishydroxymethylphosphine forms tris-2-cyanoethylphosphine[88]:

$$P(CH_2OH)_3 \xrightarrow[H_2O]{CH_2=CH-CN} [(HOCH_2)_3\overset{+}{P}CH_2CH_2CN]\,\overline{OH} \xrightarrow[-(CH_2O+H_2O)]{} (HOCH_2)_3PCH_2CH_2CN$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$(HOCH_2)P(CH_2CH_2CN)_2 \xrightarrow[-(CH_2O+H_2O)]{CH_2=CHCN} [HOCH_2\overset{+}{P}(CH_2CH_2CN)_2]\,\overline{OH} \rightarrow P(CH_2CH_2CN)_3.$$

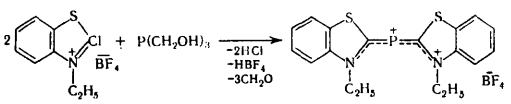
Trishydroxymethylphosphine reacts with butylsulphenyl chloride and with diethylchloramine to form quaternary phosphonium salts[89]:

$$P(CH_2OH)_3 \xrightarrow{C_4H_9SCl} \left[\begin{matrix} P(CH_2OH)_3 \\ | \\ SC_4H_9 \end{matrix}\right]^+\overline{Cl}$$

$$P(CH_2OH)_3 \xrightarrow{(C_2H_5)_2NCl} \left[\begin{matrix} P(CH_2OH)_3 \\ | \\ N(C_2H_5)_2 \end{matrix}\right]^+\overline{Cl}.$$

Quaternary phosphonium salts are recommended for use as additives in lubricating oils and as flame-resistant finishes for textiles[75], and also as pesticides and fungicides[21,23].

Trishydroxymethylphosphine has been used to prepare new coloured compounds, phosphamethincyanines, containing tervalent phosphorus having a coordination number of 2. Thus, in the presence of ethyldi-isopropylamine, 2-chloro-*N*-ethylbenzothiazole fluoroborate and trishydroxymethylphosphine gave a 45% yield of phosphamethincyanine[90]:



Other symmetrical and unsymmetrical phosphamethincyanines have been obtained in a similar manner.

Like alcohols, hydroxymethylphosphines are able to form alkoxides on treatment with metallic sodium[17]:

$$RP(CH_2OH)_2 + Na \rightarrow RP(CH_2ONa)_2 + H_2$$

where R = alkyl.

With diethylamine, hydroxymethylphosphines form aminomethylphosphines[89]:

$$R_nP(CH_2OH)_{3-n} \xrightarrow{HN(C_2H_5)_2} R_nP[CH_2N(C_2H_5)_2]_{3-n}$$

where n = 0–2 and R = alkyl. The products are able to react with compounds containing labile hydrogen[90]. Compounds of a similar type are obtained also by the action of secondary amines on tetrakishydroxymethylphosphonium chloride[91]:

$$[P(CH_2OH)_4]^+\overline{Cl} + 4HNR_2 \rightarrow (R_2NCH_2)_3P + CH_2O + R_2NH\cdot HCl$$

where R = alkyl, allyl or R_2N = morpholino; by the action of formaldehyde on phosphine and phosphines in the presence of secondary amines[92] or amides[93]:

$$R_{3-n}PH_n + nCH_2O + nHNR'_2 \rightarrow (R'_2NCH_2)_nPR_{3-n} + nH_2O$$

where n = 0–2 and R,R′ = alkyl; and also from the reaction between primary phosphines and tetraethylmethylenediamine[89]:

$$C_6H_5PH_2 + 2(C_2H_5)_2NCH_2N(C_2H_5)_2 \rightarrow C_6H_5P[CH_2N(C_2H_5)_2]_2 + 2(C_2H_5)_2NH.$$

Esters of hydroxymethylphosphines are formed by the action of acylating agents on hydroxymethylphosphines or their sodium salts[17,68]:

$$\left.\begin{matrix} R_2PCH_2OH \\ R_2PCH_2ONa \end{matrix}\right\} \xrightarrow{R'COCl} R_2P(CH_2OCOR').$$

These compounds are obtained also by the alkaline decomposition of the corresponding acylated quaternary phosphonium salts[94,95]:

$$[R_nP(CH_2OCOCH_3)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2OCOCH_3)_{3-n}$$

where n = 0–2 and R = alkyl.

Cases are unknown in which ethers have been obtained directly from hydroxymethylphosphines. The alcoholysis of trischloromethylphosphine results in formation of the methylbisalkoxymethylphosphine oxide[51,96]:

$$(ClCH_2)_3P \xrightarrow[ROH]{RONa} CH_3\overset{O}{\overset{\|}{P}}(CH_2OR)_2.$$

Hydroxymethylphosphines isomerise when heated. Thus methyldicyclohexylphosphine oxide has been obtained from dicyclohexylhydroxymethylphosphine[52]:

$$(\text{cyclo-}C_6H_{11})_2PCH_2OH \xrightarrow[3\text{ h}]{240-250^\circ} (\text{cyclo-}C_6H_{11})_2\overset{O}{\overset{\|}{P}}CH_3 + (\text{cyclo-}C_6H_{11})_2PH + CH_2O$$

40.5% 49.5%

and alkylphosphine oxides from 1-hydroxyalkyldiphenylphosphines on boiling in acetic acid in the presence of toluene-*p*-sulphonic acid[62]:

$$(C_6H_5)_2\underset{\underset{OH}{|}}{PCH}-R \xrightarrow[CH_3-C_6H_4-SO_3OH]{CH_3COOH} (C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2R$$

where R = H, alkyl, phenyl.

The chemical properties of hydroxymethylphosphonium salts and bases, unlike those of hydroxymethylphosphines, are determined solely by the hydroxymethyl groups. These groups in the quaternary salts can be acylated by acid chlorides[94,95] or acid anhydrides[52]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{X} \rightarrow [R_nR(CH_2O\overset{O}{\overset{\|}{C}}R')_{4-n}]^+\overline{X}$$

where n = 0–3 and R, R′ = alkyl, aryl. They can be converted into chloromethyl groups by the action of phosphorus pentachloride[2,97] or thionyl chloride[52,54,63,97]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{Cl} \xrightarrow{SOCl_2(PCl_5)} [R_nP(CH_2Cl)_{4-n}]^+\overline{Cl}$$

where n = 0–2 and R = alkyl, aryl; or

$$[P(CH_2OH)_4]^+\overline{OH} \xrightarrow[CCl_4]{PCl_5} (ClCH_2)_4PCl^{12,13}.$$

With phenyl isocyanate hydroxymethyltriphenylphosphonium fluoroborate forms the corresponding phenylurethane[52]:

$$[(C_6H_5)_3PCH_2OH]^+\overline{BF_4} + C_6H_5NC{=}O \rightarrow [(C_6H_5)_3PCH_2O\overset{O}{\overset{\|}{C}}NHC_6H_5]^+\overline{BF_4}$$

and with diazomethane it gives methyltriphenylphosphonium fluoroborate[52]:

$$[(C_6H_5)_3PCH_2OH]^+\overline{BF_4} \xrightarrow[-CH_2O]{CH_2N_2} (C_6H_5)_3P + \{|CH_3^+\} \rightarrow [(C_6H_5)_3PCH_3]^+\overline{BF_4}\,.$$

An interesting property of hydroxymethylphosphonium halides is their tendency to split into tertiary phosphine and phosphine oxides. For example, treatment of tetrakishydroxymethylphosphonium chloride with excess of aqueous alkali yields the tertiary phosphine oxide, hydrogen, and an aldehyde:

$$P(CH_2OH)_4Cl + NaOH \rightarrow (HOCH_2)_3P{=}O + CH_2O + H_2 + NaCl\,.$$

Trishydroxymethylphosphine oxide was first isolated by Hoffmann as the tribenzoate. It has since been found that an 80% yield of the pure oxide can be obtained from tetrakishydroxymethylphosphonium chloride by the action of barium carbonate[98,99]. However, the isolation of trishydroxymethylphosphine oxide from an aqueous solution containing a metal chloride is extremely difficult, owing to its solubility in water and its sparing solubility in organic solvents. Good results have been obtained by prolonged extraction from concentrated solutions with alcohol. Trishydroxymethylphosphine oxide is obtained also by the action of lead carbonate in propan-1-ol on tetrakishydroxymethylphosphonium chloride[100].

When trishydroxymethylphosphine oxide is treated with alkalis under more severe conditions, a molecule of hydrogen is split off, and salts of phosphinic acids are formed:

$$P(O)(CH_2OH)_3 \xrightarrow{NaOH} \underset{\underset{ONa}{|}}{P(O)(CH_2OH)_2}\,.$$

Bishydroxymethylphosphinic acid can be obtained from tetrakishydroxymethylphosphonium chloride by boiling the latter with alkali or with sodium carbonate[98]:

$$(HOCH_2)_4PCl + Na_2CO_3 + 3H_2O \rightarrow 3\,(HOCH_2)_2P\!\!\underset{OH}{\overset{O}{\diagup}} + 4CH_2O + 4H_2 + 2NaCl + CO_2$$

or by heating sodium hypophosphite with paraform and then acidifying the product with an acid[101]:

$$NaH_2PO_2 + nCH_2O \rightarrow \underset{\underset{OH}{|}}{\overset{O}{\overset{\|}{P}}(CH_2OH)_2}\,.$$

Alkyltrishydroxymethylphosphonium halides are decomposed by excess of aqueous alkali with the formation of tertiary phosphine oxides. Thus treatment of propyltrishydroxymethylphosphonium chloride with barium hydroxide octahydrate at 60°C gives propylbishydroxymethylphosphine oxide[63]:

$$[C_3H_7P(CH_2OH)_3]^+\overline{Cl} \xrightarrow{Ba(OH)_2\cdot 8H_2O} \underset{\underset{O}{\|}}{C_3H_7P(CH_2OH)_2}\,.$$

Hydroxymethylphosphine oxides can be acylated by the ethyl esters[68] and by the chlorides[2,63,68,102-104] of carboxylic acids, when one, two, or three hydroxymethyl groups may react:

$$\underset{\underset{O}{\|}}{R_nP(CH_2OH)_{3-n}} \xrightarrow{RCOCl} \underset{\underset{O}{\|}}{R_nP(CH_2OCOR)_{3-n}}$$

where n = 0–2 and R = alkyl, aryl. The reaction of hydroxymethylphosphine oxides with thionyl chloride[52,63] and with phosphorus pentachloride[70] yields chloromethylphosphine oxides:

$$\underset{\underset{O}{\|}}{R_nP(CH_2OH)_{3-n}} \xrightarrow{PCl_5(SOCl_2)} \underset{\underset{O}{\|}}{R_nP(CH_2Cl)_{3-n}}$$

where n = 0–2 and R = alkyl, aryl.

Tetrakishydroxymethylphosphonium chloride and alkyl(aryl)hydroxymethylphosphonium halides are decomposed by the calculated quantities of alkali[53,62,68], alcoholic alkali[53,68], or sodium ethoxide[53] to tertiary hydroxymethylphosphines¶:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2OH)_{3-n} + CH_2O + NaCl$$

where n = 0–2 and R = alkyl, aryl. The decomposition of bis-1-hydroxyalkyldiphenylphosphonium chlorides by aqueous alkalis is accompanied by side-reactions, which lower the yields of 1-hydroxyalkyldiphenylphosphines[61].

The action of tertiary amines on hydroxymethylphosphonium halides also splits off formaldehyde, to give good yields of tertiary phosphines[73,76]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{Cl} \xrightarrow[-(C_2H_5)_3N\cdot HCl]{(C_2H_5)_3N} R_nP(CH_2OH)_{3-n}$$

where n = 0–2 and R = alkyl, aryl.

The alkylation of hydroxymethylphosphines and the dealkylation of hydroxymethylphosphonium halides yield tertiary hydroxymethylphosphines and phosphines containing no hydroxymethyl groups[52,62,73,76], dialkylamides of bishydroxymethylphosphinous acid[89]:

$$[RP(CH_2OH)_3]^+\overline{X} \xrightarrow{\overline{B}} RP(CH_2OH)_2 \xrightarrow{R'X} [RR'P(CH_2OH)_2]^+\overline{X} \xrightarrow{\overline{B}}$$

$$\rightarrow RR'P(CH_2OH) \xrightarrow{R''X} [RR'R''P(CH_2OH)]^+\overline{X} \xrightarrow{\overline{B}} RR'R''P$$

where R = alkyl, aralkyl, dialkylamino and $\overline{B}$ = NaOH, $(C_2H_5)_3N$, and also diphosphines[82,107]:

$$\left[\begin{matrix} R_2\overset{+}{P}-(CH_2)_n-\overset{+}{P}R_2 \\ | \qquad\qquad | \\ CH_2OH \qquad CH_2OH \end{matrix}\right] 2\overline{X} \xrightarrow[-(2CH_2O+2NaCl)]{\text{conc. NaOH}} R_2P(CH_2)_nPR_2.$$

Tertiary amines proved to be unsuitable for the decomposition of diphosphonium salts.

Alkylenediphosphine oxides can be obtained by the oxidation of alkylenediphosphines†.

IV. PREPARATION OF PHOSPHORUS-CONTAINING POLYMERS BASED ON TETRAKISHYDROXYMETHYLPHOSPHONIUM CHLORIDE AND ITS DERIVATIVES

In contrast to phosphorus-containing insecticides, plasticisers, lubricating-oil additives, etc., organophosphorus polymers have not hitherto found wide application.

¶ The action of alkalis on chloromethylphosphonium halides similarly yields chloromethylphosphines[2,52,54,70,105]:

$$[R_nP(CH_2Cl)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2Cl)_{3-n} + nCH_2O + NaCl + H_2O$$

where n = 0–2, R = alkyl, aryl, and X = Cl, BF_4. However, side-reactions are also possible, which considerably diminish the yield of tertiary phosphines. When, for example, tetrakischloromethylphosphonium chloride is boiled, methylbischloromethylphosphine oxide is formed[106]:

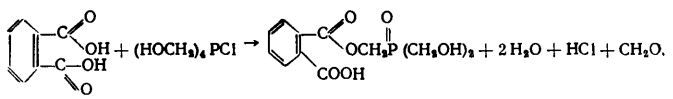
$$[P(CH_2Cl)_4]^+\overline{Cl} \xrightarrow{NaOH} \underset{\underset{O}{\|}}{CH_3P(CH_2Cl)_2}\,.$$

† Alkylenediphosphine oxides are known to be effective extractants for the recovery and separation of rare-earth metals[108-110]. Until now, however, they have been relatively difficultly accessible compounds[107,111-126].

However, available data indicate that several of them, possessing specific properties, may be of practical interest. Thus great attention is being paid to the search for phosphorus-containing polymers suitable for surface coatings on metals and for impregnating various materials in order to confer on them in some cases corrosion-resistance and in others non-flammability.

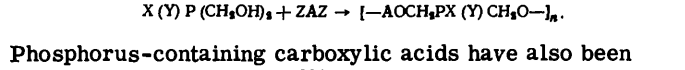
Such polymers can be obtained from tetrakishydroxymethylphosphonium chloride‡, trishydroxymethylphosphine oxide, bishydroxymethylphosphinic acid, alkyl(aryl)bishydroxymethylphosphines, and the corresponding phosphine oxides. The hydroxymethyl groups confer on these substances the properties of alcohols and aldehydes (in particular formaldehyde). Therefore they can be employed on the one hand as glycols for the preparation of polyesters (by polyesterification with dibasic acids, by the transesterification of esters, or by the alcoholysis of amides of phosphorus acids) and on the other as the phosphorus component for the production of high polymers by condensation with nitrogen-containing compounds and with phenols.

Tetrakishydroxymethylphosphonium chloride and bishydroxymethylphosphinic acid react with numerous carboxylic acids and their anhydrides to form phosphorus-containing polymers resembling alkyd resins[99,128-131]. The reaction involves the intermediate formation of monomeric substances of the following structure:



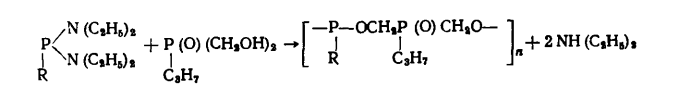
With dibasic acids the final products are fusible, transparent resins, probably of linear structure, and possessing self-extinguishability. With sebacic acid, for example, a rubberlike elastic polymer is obtained, showing good compatibility with polyethylene and conferring self-extinguishing properties on the latter; citric, succinic, phthalic, and adipic acids yield viscous liquids or brittle solids. These resins can be used for the production of corrosion-resistant films on metal surfaces.

Phosphorus-containing esters are obtained by the polycondensation of alkylbishydroxymethylphosphines and the corresponding oxides and sulphides with dicarboxylic acids or their esters, anhydrides, or chlorides[132,133]:



Phosphorus-containing carboxylic acids have also been subjected to this reaction[134].

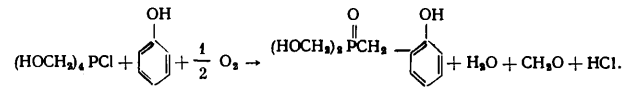
Alcoholysis of the tetraethyldiamides of methylphosphonous and phenylphosphonous acids with propylbishydroxymethylphosphine oxide gives polymers of the following type[134]:



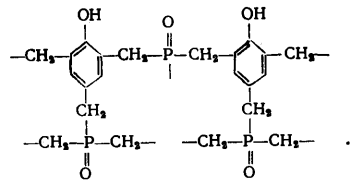
where R = alkyl, aryl. The polymers are semi-solid resinlike substances (especially those from phenylphosphonous tetraethyldiamide) having molecular weights up to 18 000. The low softening points (30–50°C) are probably due to the high phosphorus contents of the polymer molecules.

‡ When tetrakishydroxymethylphosphonium chloride is heated at 150–200°C, liquid polymers are formed which can be used for the impregnation of cellulosic materials to make them non-flammable[127].

Tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide[135], and alkylbishydroxymethylphosphines react through their hydroxy-groups with phenols, water being eliminated and phosphorus-containing polymers of linear and network structure being formed (hydroxymethyl- and bishydroxymethyl-phosphinic acids, in contrast, form not phosphorus-containing polymers but phenol–formaldehyde resins when heated with phenol[136]). Phenols containing a hydrogen atom in position 2, 4, or 6 undergo this reaction. Substituents in the phenols exert a similar influence on the condensation as in the case of the interaction of phenols with formaldehyde. Whereas the interaction of formaldehyde and phenols involves the intermediate formation of a hemiacetal[137], the condensation of tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines with phenols obviously occurs directly at the *ortho*- and *para*-positions in the phenols, and thus bypasses the stage of semiacetal formation[131,138-143]:



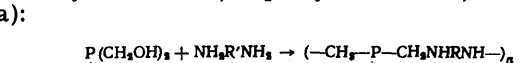
The linear polycondensation products formed initially are converted into resins of complicated three-dimensional structure only when three active centres are present in the phenols employed (phenol, resorcinol, phloroglucinol)[18,140]:



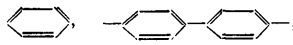
If, however, the *para*-position or one of the *ortho*-positions of the phenol is occupied by a substituent, soluble, fusible resins of linear structure are formed (with *o*-bromophenol, quinol, pyrogallol, catechol)[140,144].

A more detailed study has been made of the properties of polymers based on alkylbishydroxymethylphosphines. These polymers possess ion-exchange properties in alkaline solution. For example, the polymer prepared from propylbishydroxymethylphosphine and phenol in equimolecular proportions has an ion-exchange capacity of 0.7 mg-equiv. g^{-1}.

Tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines also condense readily, with the liberation of water, with various nitrogen-containing compounds[3,131,134,138,142-158]. Linear polyaminomethylenephosphines are formed from alkylbishydroxymethylphosphines and diamines (hexamethylenediamine, *p*-phenylenediamine, benzidine, urea):



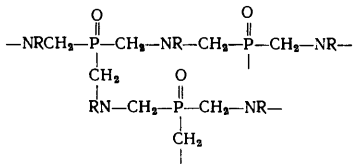
where R = alkyl and R′ = $[CH_2]_6$,



The resulting polymers (M = 42 900–54 000) are solids, mostly amorphous powders, soluble neither in acids nor in alkalis.

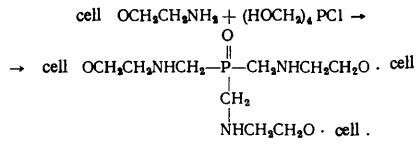
With amines (hydrazine, hydroxylamine, hexadecylamine, etc.) tetrakishydroxymethylphosphonium chloride and trishydroxymethylphosphine oxide initially form water-soluble linear products $(HOCH_2)_2POCH_2NHR$, which set on

standing in the cold for a few hours or on being heated to 100–150°C for a few minutes, to give strongly branched polymers having the structure



With ammonia and melamine tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines form branched polymers in the form of incombustible powders, insoluble in the usual solvents.

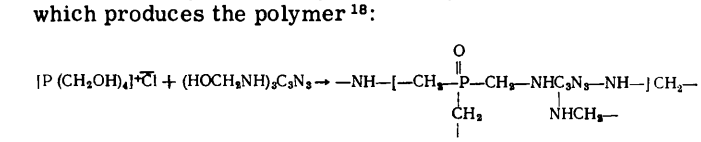
The flameproofing action of polymers obtained from tetrakishydroxymethylphosphonium chloride and amines was first discovered in a study of the properties of aminated cotton[18]. The quaternary chloride reacts with the amino-group in the aminated cotton to form a non-flammable modification of cellulose:



The phosphorus introduced into the cellulose in this way is firmly bound, and is not removed by boiling in water.

In order to confer flame-resistance on cotton without aminating it, tetrakishydroxymethylphosphonium chloride is made to react with amines, e.g. melamine, urea, thiourea, hydroxymethylmelamine. The phosphonium chloride condenses with these compounds, to form an insoluble resin on the fibre. Dicyandiamide, guanidine, melamine, and their hydroxymethyl derivatives form with tetrakishydroxymethylphosphonium chloride three-dimensional polymers, which in the cold do not dissolve in water, acids, or alkalis. The best results are obtained by condensing the quaternary chloride on the cellulosic materials with hydroxymethyl derivatives of melamine.

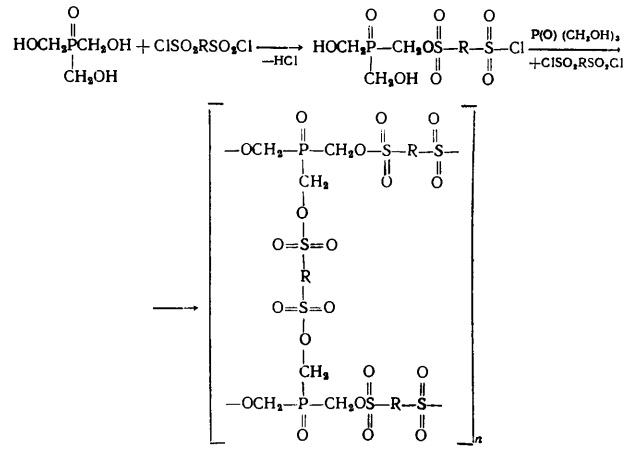
The following recipes—(1) 1868 g of tetrakishydroxymethylphosphonium chloride + 1338 g of trishydroxyethylamine + 1800 g of water; (2) 1060 g of trishydroxymethylmelamine + 1114 g of urea + 5062 g of water—have been proposed for giving cotton fabrics a non-flammable finish. Before use the two solutions are thoroughly mixed, and then applied to the fabric. The principal components of these recipes are tetrakishydroxymethylphosphonium chloride and trishydroxymethylmelamine, interaction between which produces the polymer[18]:



As a result of impregnation and a special treatment the fabric increases in weight by ~ 17%, and withstands the standard test for flame-resistance. The impregnated fabric retains its flame-resistance after 15 washes, and becomes crease-resistant and rotproof.

Copolymers obtained by the polycondensation of tetrakishydroxymethylphosphonium chloride with phenols and nitrogen compounds have also been proposed[145,159] for coating and impregnating fabrics and wood in order to confer on them non-flammable properties.

Phosphorus-containing polysulphonates are obtained by the interaction of aromatic disulphonyl chlorides with tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and trishydroxymethylphosphine[160]:



Tetrakishydroxymethylphosphonium chloride and trishydroxymethylphosphine oxide also find application for addition to other polymers with the aim of conferring on the latter various valuable properties, e.g. for the production of epoxide resins having improved heat-resistance[161], as modifiers in epoxide resins[156], as inhibitors of discoloration in film-forming compositions[162], etc.

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U. D. C. 547.313 : 547.414.7

Nitrosochlorination of Alkenes

P.P.Kadzyauskas and N.S.Zefirov

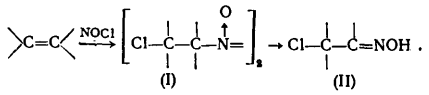
The reaction of nitrosochlorination has recently been attracting the attention of organic chemists, since it provides a ready means of obtaining classes of compounds which are extremely interesting from both theoretical and practical points of view. The laws governing this reaction, including the fine details of the stereochemistry and mechanism of this reaction, have not hitherto been systematised. The present review gives a detailed and systematic survey of the processes involved in nitrosochlorination and of the empirical laws of this reaction. Special attention is paid to published data on the mechanism and the stereochemistry of the reaction; nitrosochlorination is shown to possess features common to other reactions of electrophilic addition. The paper is addressed to a wide circle of organic chemists and undergraduate and postgraduate students. The list of references contains 119 items.

CONTENTS

Introduction 544
1. Products of normal nitrosochlorination 544
2. General features of the normal nitrosochlorination of alkenes 545
3. Mechanism and stereochemistry of the nitrosochlorination of alkenes 546
4. Anomalous products of nitrosochlorination 548

INTRODUCTION

In 1877 Tilden[1] established that nitrosyl chloride adds at a double bond to form dimeric nitrosochlorides of the type (I), which are able to isomerise to the corresponding oximes (II):



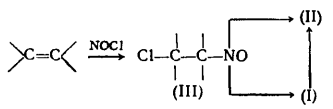
This reaction played an important part in the study of terpene compounds.

Nitrosochlorination has recently attracted the attention of chemists as a method of synthesising aziridine derivatives[2], intermediates in the synthesis of amino-sugars[3,4], amino-steroids[5-7], etc.

Several reviews have been published on methods of preparation, properties, and reactions of nitrosyl chloride[8-12]. The last review[12] covers all publications up to 1949, and fully reveals the preparative value of these reactions. During recent years, however, a large number of papers have appeared which change fundamentally our ideas on the mechanism and the stereochemistry of the nitrosochlorination of alkenes. In our survey, therefore, we have tried to summarise the general features of this reaction, while paying special attention to the stereochemistry and the mechanism of the process. We have used mainly literature which has appeared since 1950, but where necessary reference has been made to earlier work.

1. PRODUCTS OF NORMAL NITROSOCHLORINATION

Tilden[1] was the first to show that compounds containing a carbon–carbon double bond react with nitrosyl chloride usually with the formation of nitrosochlorides (III), which are dark blue oily substances. In most cases the latter are converted further into white crystalline substances—hydroxyimino-compounds (II)—or even into dimeric compounds (I). Henceforward we shall term the reaction leading to compounds of types (I), (II), or (III) normal nitrosochlorination:



It is readily seen that isomerisation to an oxime is possible only in those nitrosochlorides in which hydrogen is attached to the carbon linked to the nitroso-group.

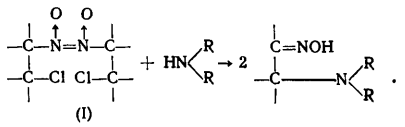
Partial conversion of (III) into (II) or into (I) can occur in the preparation of nitrosochlorides[13-16] or during their recrystallisation[17]. This explains the discrepancies in the early published data on the reaction products obtained from nitrosyl chloride and alkenes. For example, several of the compounds obtained earlier, which were regarded as hydroxyimino-compounds[15,18], have subsequently proved to be dimeric compounds[16,19].

The structure of dimeric nitrosochlorides was for a long time a matter of controversy. The work of Gowenlock[20-23] and also of Smith[24] showed that the dimerisation of nitroso-compounds involves formation of the grouping $-N(\rightarrow O)=N(\rightarrow O)-$. In such a case *syn–anti* isomerism may be expected to appear about the N=N bond even in the nitrosochlorides (in the literature on nitrosochlorination this isomerism is frequently termed *cis–trans* isomerism, although this name is evidently not accurate, and sometimes[25] incorrect terminology leads to misunderstanding).

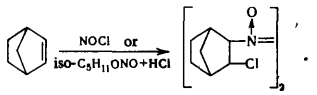
As several workers have shown, the nitrosochlorination of alkenes actually results in the formation of both *syn*- and *anti*-forms of dimeric nitrosochlorides (with respect to the N=N bond)[25-29]. In most cases the *syn*-isomers are unstable, and are readily isomerised into the *anti*-isomers. In several cases such isomerisation can occur so readily that the *syn*-isomers cannot be isolated at all[29-31].

In the molten form or in a hot solvent dimeric nitrosochlorides are in equilibrium with the monomeric form, as is indicated by the dark blue colour of the solution. After prolonged boiling, however, the hydroxyimino-compound (II) can be isolated from solutions of the dimeric nitrosochlorides[17,32,33]. The best method for obtaining oximes is probably to boil the dimeric nitrosochlorides with dilute hydrochloric acid[32,34].

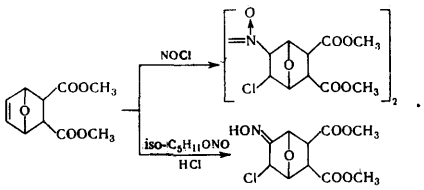
Dimeric nitrosochlorides (I) are decomposed with the formation of oximes by the action of primary or secondary amines[34-37], alkoxides[16,35], or metal phenyl sulphides[37]:



The course of the reaction is substantially influenced by the way in which nitrosochlorination is conducted. Differing results are obtained depending on whether the alkene is treated with pure nitrosyl chloride, with nitrosyl chloride contaminated with hydrogen chloride, or with isopentyl nitrite and hydrochloric acid. Thus the nitrosochlorination of norbornene and norbornadiene, both with pure nitrosyl chloride and with isopentyl nitrite and hydrochloric acid, results in the formation only of dimeric nitrosochlorides[38-40]:



In the nitrosochlorination of dimethyl 7-oxabicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylate, however, pure nitrosyl chloride yields the dimer, whereas the use of isopentyl nitrite and hydrochloric acid gives the hydroxyimino-compound[32,41]:



It is seen from this example that even slight differences in the structure of the alkene strongly affect the course of the reaction.

Sometimes normal nitrosochlorination takes place only in the presence of a catalyst, such as nickel chloride, iron(II) chloride, copper(I) chloride[42], or aluminium chloride[43,44]. Thus ethylene and propene[45] do not form nitrosochlorides on reaction with nitrosyl chloride under the usual conditions of nitrosochlorination. However, good yields of the corresponding nitrosochlorides have been obtained[42] in dichloromethane or in chloroform in the presence of a catalyst (Raney nickel).

2. GENERAL FEATURES OF THE NORMAL NITROSOCHLORINATION OF ALKENES

The nitrosochlorination of unsaturated hydrocarbons shows several general features associated with the effect of substituents adjacent to the carbon–carbon double bond. Published data indicate that nitrosyl chloride adds to alkenes at the double bond more readily the more nucleophilic is this bond. Thus nitrosochlorination takes place more easily with di- and tri-substituted alkenes[13,15,16,18,27,46-51] than with monosubstituted alkenes[50-52].

It is noteworthy that the possibility and the rate of nitrosochlorination depend substantially on the position of the carbon–carbon double bond in the chain. Thus Ogloblin and his coworkers were unable to isolate crystalline dimeric nitrosochlorides by the nitrosochlorination of but-1-ene[52], pent-1-ene, hex-1-ene, hept-1-ene, or oct-1-ene[50], and only in the case of non-1-ene can stable dimeric compounds be obtained[12]. It is interesting to note that nitrosyl chloride reacts with propene at −22°C, whereas with ethylene the reaction is conducted in a nickel autoclave at +40°C.[42]

However, on treating but-2-ene[48] in contrast to but-1-ene with nitrosyl chloride, Ogloblin and Samartsev obtained a 29% yield of a crystalline dimer. Tilden and Forster[53], and subsequently also Thorne[54], isolated monomeric nitrosochlorides of hex-2-ene, hept-2-ene, oct-2-ene, and 4-methylpent-2-ene in low yields. Nevertheless, on the basis of a study of the infrared spectra, Ogloblin and Samartsev consider that pent-2-ene[27] and hex-2-ene[28] form dimeric compounds, though these are liquids.

The course of the reaction is probably unaffected by conjugation of the double bond with a benzene ring. Thus propenylbenzene forms a nitrosochloride[54], whereas allylbenzene does not react with nitrosyl chloride. Similarly, 1,3,5-trimethylstyrene does not interact with nitrosyl chloride[54], whereas 1,3,5-trimethyl-2-propenylbenzene[55] gives a crystalline nitrosochloride.

Nitrosyl chloride adds readily also to cycloalkenes to

Nitrosyl chloride adds readily also to cycloalkenes to form the normal nitrosochlorination products. For example, cyclohexene[25,26,56-60], cyclo-octene[61], cyclododecatriene[62-64], Δ^9-octahydronaphthalene[65-67], dicyclopentadiene[68], and *endo*- and *exo*-2-oxa-1,2-dihydrodicyclopentadienes[69] readily form dimeric chloro-nitroso-derivatives.

Nitrosochlorination goes still better with alkenes containing more than one alkyl substituent adjacent to the double bond. Thus 2-methylpropene[16,70] and 2-methylbut-2-ene[17,45-47,54] form with nitrosyl chloride dimeric compounds in yields of 60% and 50% respectively. 2,3,3-Trimethylbut-1-ene, 2-methylbut-1-ene, and 2-*p*-tolylpropene give yields respectively of 28%, 19%, and 9% of crystalline dimeric compounds[50]. 2,4,4-Trimethylpent-1(and 2)-enes also give good yields of dimeric nitrosochlorides[54].

A monomeric derivative was isolated from reaction of the tetrasubstituted 2,3-dimethylbut-2-ene with nitrosyl chloride[71]. In this case formation of a dimeric compound is probably made difficult by steric hindrance.

The addition of nitrosyl chloride obeys the Markovnikov rule[15,18,27,28,33,48,50,53,72-75]: the nitroso-group adds to the most hydrogenated carbon atom, which indicates that the double bond is initially attacked by the nitrosyl cation[73].

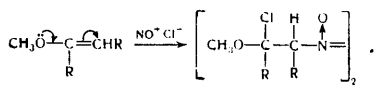
The orienting effect of n-alkyl substituents on the addition of nitrosyl chloride is the same as that of the methyl group. In the case of branched alkyl substituents the nitroso-group adds preferentially to a carbon atom attached to methyl[28], which is explained by the inductive effect of the alkyl groups. The strengthening of the orienting effect of various alkyl groups compared with that of methyl corresponds to the increase in the positive inductive effect of these groups[28], in the sequence $CH_3 < C_2H_5 < CH(CH_3)_2 < C(CH_3)_3$.

Recent kinetic investigations[76] indicate that electron-donor groups influence nitrosochlorination. The accompanying Table shows that the rate of nitrosochlorination decreases as the double bond becomes less nucleophilic.

Rate constants for the nitrosochlorination of alkenes in chloroform at 0°C.[76]

Alkene	$10^{-4}k_2$, $M^{-1}\,s^{-1}$	Alkene	$10^{-4}k_2$, $M^{-1}\,s^{-1}$
Methylallyl chloride	0.29	2,3-Dimethylbut-1-ene	20
3,3-Dimethylbut-1-ene	0.32	2-Methylpent-1-ene	23
4,4-Dimethylpent-1-ene	0.52	β-Methylstyrene	26
cis-Stilbene	0.64	Cyclohexene	29
3-Methylbut-1-ene	0.69	2-Methylpropene	30
3-Methylpent-1-ene	1.0	2-Methylbut-1-ene	33
4-Methylpent-1-ene	1.2	But-2-ene	52
But-1-ene	1.5	Hex-3-ene	66
Hex-1-ene	1.6	*cis*-Pent-2-ene	77
Oct-1-ene	1.8	*trans*-Pent-2-ene	108
Dodec-1-ene	1.8	Cycloheptene	135
trans-Stilbene	2.9	Cyclopentene	>1000
Styrene	6.5	2-Methylbut-2-ene	>1000
1,1-Diphenylethylene	9.8	2,3-Dimethylbut-2-ene	>1000
α-Methylstyrene	17	Norbornene	>1000

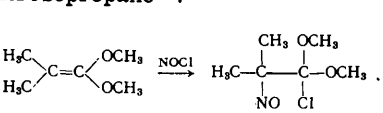
The nucleophilic character of the double bond is enhanced also in vinyl ethers owing to the effect of conjugation between the oxygen electrons and the π-electrons of the double bond. Such compounds therefore react vigorously with nitrosyl chloride[30,77]:



On the other hand, allyl methyl ether, where conjugation of this type is absent, does not form normal nitrosochlorination products[19].

Methylated and methoxylated styrenes give higher yields of the crystalline dimeric nitrosochlorides than do the unsubstituted styrenes. Thus the nitrosochlorination of α-methylstyrene[54], *p*-methylstyrene[45,56,57], *o*-methylstyrene[54], and *m*-methylstyrene[54] gave 71%, 66%, 52%, and 32% respectively of the dimers, whereas unsubstituted styrene[45,54,56,57] forms only 30% of the dimeric compound.

The nucleophilic character of the carbon–carbon double bond in the acetals of ketens is still more intensified by the electron-donor effect of the two alkoxy-groups. In this case, therefore, nitrosochlorination is rapid, and is probably immediately followed by instantaneous isomerisation of the nitrosochloride into an oxime[78]. As Ogloblin and his coworkers have shown[78], nitrosyl chloride easily interacts also with 1,1-dimethoxy-2-methylpropene, but the sole product of this reaction is 1-chloro-1,1-dimethoxy-2-methyl-2-nitrosopropane[78]:



On the other hand, electron-acceptor substituents in the α-position with respect to the double bond strongly retard nitrosochlorination[54,72,79]. Thus maleic and fumaric acids are recovered unchanged[53] from treatment with nitrosyl chloride. Similarly, crotonic and vinylacetic acids[53] also

do not react with nitrosyl chloride, but on prolonged treatment in sealed tubes are decarboxylated[44].

According to Thorne neither 5-phenylpent-4-enoic nor 6-phenylhex-5-enoic acid forms a nitrosochloride[54], although in the former case the double bond is separated from the carboxyl by two methylene groups. Published data do not indicate what is the minimum number of methylene groups necessary between the double bond and the carboxyl for reaction to occur. However, it is known that oleic acid does form a nitrosochloride[53,80].

An ester group has a similar effect. Thus Ogloblin and Semenov were unable to obtain a nitrosochloride by the action of nitrosyl chloride on methyl acrylate[81] or methyl methacrylate[44].

Chlorinated ethylenes do not form nitrosochlorides because of the strong influence of the chlorine atom[43,72,79,82,83].

The presence of a nitro-group near the double bond also prevents nitrosochlorination. Thus neither β-nitrostyrene[54] nor 2-nitropropene[83] gives a normal nitrosochlorination product.

Ogloblin and Potekhin showed[84-86] that, with αβ-unsaturated ketones, nitrosochlorination goes fairly smoothly, in spite of the presence of a strong electron-acceptor group. It is interesting that a dimer or an oxime is obtained depending on the reaction conditions or the structure of the αβ-unsaturated ketone[87,88].

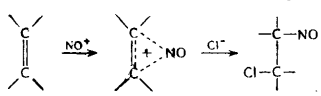
Nitrosochlorination also takes place relatively easily in the presence of a nitrile group. As Ogloblin and Semenov showed, at ordinary temperatures acrylonitrile gives β-chloro-α-hydroxyiminopropionitrile (yield 48%):[81]

$$CH_2{=}CH{-}CN \xrightarrow{NOCl} \underset{Cl}{\overset{}{CH_2{-}C{-}CN}} \underset{NOH}{\overset{}{\parallel}} .$$

3. MECHANISM AND STEREOCHEMISTRY OF THE NITROSOCHLORINATION OF ALKENES

As already stated above, the addition of nitrosyl chloride follows the Markovnikov rule, which indicates that the nitroso-group adds as an electrophilic species in the form of the nitrosyl cation.

On this Ingold[73] suggested that the reaction of nitrosyl chloride with alkenes took place according to the scheme



which is usual for electrophilic additions at a double bond. According to this, nitrosochlorination should result in the formation of *trans*-addition products. An analogous mechanism has been suggested in several other papers[30,43,54,75,77-78,89]. It must be emphasised, however, that the stereochemistry of the reaction has not been studied in any of the work on the addition of nitrosyl chloride to a double bond, with the exception of a few recent investigations[3-7,32,67].

The proposed mechanism is consistent with results for the infrared spectra[90], the electrical conductivity of the solutions[10,91-93], and isotopic exchange in liquid nitrosyl chloride[94-97], from which it follows that nitrosyl chloride dissociates according to the equation†:

$$NOCl \rightleftarrows NO^+ + Cl^- .$$

The concentration of the chloride ion and hence of the nitrosyl cation is 10^{-8} g-ion litre^{-1} at 18°C.[45]

† It must be remarked that sometimes the unjustified opinion is expressed that nitrosyl chloride dissociates into a chlorine cation and a nitrosyl anion[98].

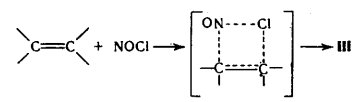
Kinetic investigations of the rate of nitrosochlorination have shown that overall it is of the second order, being of the first order with respect to each component. In the nitrosochlorination of styrene and cyclohexene in various solvents[76] the following sequence of reaction velocity

$$CH_3OH < (C_2H_5)_2O < CCl_4 < C_6H_5CH_3 \simeq n\text{-}C_7H_{16} < C_6H_5Cl < C_6H_4Cl_2 < C_6H_5CN < CH_2Cl_2 < C_6H_5NO_2 < CHCl_3$$

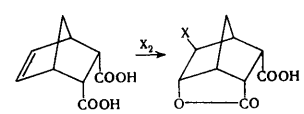
has been observed, which is difficult to explain. Unfortunately, no published data are available on the rate of reaction in liquid sulphur dioxide, where recent work[99] has shown that the course of the reaction is probably most unambiguous.

Nitrosochlorination is characterised by high entropies of activation: thus the values for styrene in chloroform and for cyclohexene are respectively −43.0 and −36.9 cal mole^{-1} deg^{-1}.[76] Unfortunately, data are lacking on the entropy of activation for nitrosochlorination in sulphur dioxide, which makes it impossible to compare the kinetic data with results of a stereochemical study (see below).

All this suggests that the transition state of the reaction is characterised by a definite and rigid orientation of the alkene and nitrosyl chloride molecules, and provides indirect evidence of the possibility of cyclic transfer of electrons, e.g. according to the scheme



There are also several experimental facts showing that nitrosochlorination does not always occur as a two-stage electrophilic addition at the double bond. It is well known that electrophilic addition to *endo*-carboxylic derivatives of norbornene involves the carboxyl and results in the formation of lactones[100,101]. For example, bromination of *endo*-adducts of diene synthesis from cyclopentadiene and maleic anhydride takes place according to the scheme

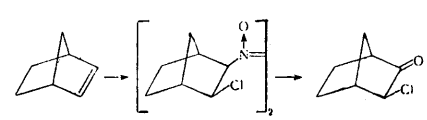


An analogous scheme is valid not only for bromination but also for the addition of mercury salts[102], 2,4-dinitrophenylsulphenyl chloride[103,104], and water[105], for opening an epoxide ring[106], etc.

Nevertheless, the interaction of *endo*-norbornenecarboxylic acid either with isopentyl nitrite and hydrochloric acid or directly with nitrosyl chloride results in the formation of dimeric nitrosochlorides, not lactones[38,67].

It should be noted that the nitrosochlorination of norbornene does not involve skeletal rearrangement of the Wagner–Meerwein type, while that of norbornadiene does not involve the second double bond[38,39].

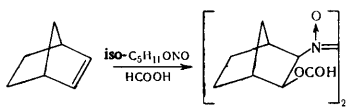
In 1964 Meinwald et al. showed that these reactions are cases of *exo-cis*-addition[67]:



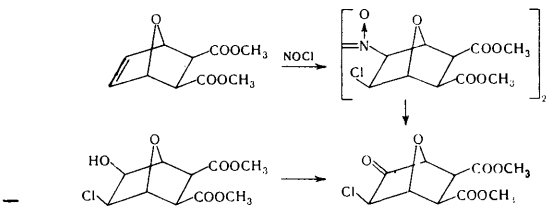
The stereochemical course of the nitrosochlorination of norbornene was elucidated by a chemical method: the dimeric nitrosochloride was converted into an *exo*-chloroketone described previously. The *cis*-configuration of the nitrosochloride of norbornene has since been confirmed by spectroscopy[3]. Miller[39] has also described the nuclear

magnetic resonance (n.m.r.) spectra, which provide unambiguous evidence of the *exo-cis*-configuration of the addition product, but he did not draw this conclusion.

It is interesting that the nitrosoformylation of norbornene[107] is also an *exo-cis*-addition:

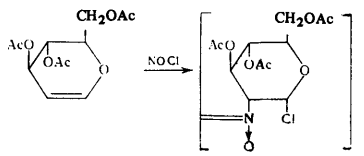


Zefirov et al. have shown[32] that the nitrosochlorination of dimethyl 7-oxabicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate proceeds as an *exo-cis*-addition. This was proved by converting the dimeric nitrosochloride into a chloroketone, which was identified by comparing it with chloroketones obtained from chlorohydrins of known configuration[108]:



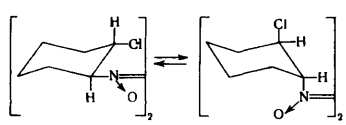
On the other hand, it has been shown in the case of hydroxymercuration[102] that the addition of weak electrophilic reagents to these bicyclic systems may lead to the formation of *cis*-addition products. Therefore it is not possible to draw general stereochemical conclusions concerning nitrosochlorination on the basis of data on the reactions of bicyclic alkenes.

The reaction of nitrosyl chloride with 3,4,6-tri-*O*-acetyl-D-glucal, 3,4-di-*O*-acetyl-D-arabinal, tri-*O*-acetyl-D-glucal, and di-*O*-acetyl-D-xylal takes place as *cis*-addition with the formation of dimeric nitrosochlorides[3,4]:



However, the stereochemical course of additions of D-glucal may also be anomalous. Thus data on the hydroxymercuration of D-glucal are contradictory: Inglis and Schwarz[109] interpret methoxymercuration as *trans*-addition, whereas results obtained by Manolopoulos et al.[110] indicate that this reaction is a *cis*-addition. The chlorination of D-glucal also takes place predominantly as *cis*-addition[3].

In this connection it is most interesting to study the stereochemistry of nitrosochlorination on simple models. Zefirov et al. have shown[111] that the reaction of cyclohexene with isopentyl nitrite and hydrochloric acid produces a dimeric nitrosochloride, which the n.m.r. spectra indicate to have a *trans*-configuration and which exists predominantly in the diequatorial form:



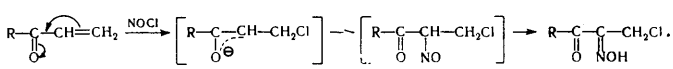
At the same time Ohno et al.[99] showed that the reaction of nitrosyl chloride with cyclohexene in liquid sulphur dioxide gives a nitrosochloride which is a *trans*-isomer. In chloroform, however, this reaction results in the formation of a dimeric nitrosochloride, to which a *cis*-configuration was attributed.

Thus the stereochemistry of nitrosochlorination depends fundamentally not only on the structure of the alkene but also on the method of preparing the nitrosochloride and on the solvent employed. The most plausible hypothesis is that the addition of nitrosyl chloride in non-polar solvents may involve an intermediate four-centre transition state. In polar solvents, however, a two-stage *trans*-addition is possible. The relative proportions of these mechanisms may depend not only on the solvent but also on the nature of the alkene, the reaction temperature, etc. It may be expected theoretically that catalysts of the aluminium chloride type will have a substantial effect on these proportions.

In 1963 Titov[43] reported the anomalous addition of nitrosyl chloride to halogenoethylenes. In order to accomplish smooth and rapid nitrosochlorination, solutions of Lewis acids (aluminium chloride, tin(IV) chloride, zinc chloride, iron(III) chloride, antimony(V) chloride) in excess of liquid nitrosyl chloride were used in this case at low temperatures. These aprotic acids form[10] with nitrosyl chloride complexes of the type $NO^+[MCl_x]^-$, which are strongly dissociated into the ions NO^+ and $[MCl_x]^-$. The use of complexes of nitrosyl chloride with Lewis acids should eliminate the possibility of a four-centre cyclic mechanism of addition of nitrosyl chloride at the double bond. Titov suggested an ionic mechanism for this process of nitrosochlorination, essentially analogous to that proposed earlier by Ingold[73].

However, data on the influence of catalysts on nitrosochlorination are contradictory. Thus Beier et al.[76] found that the use of Lewis acids produces no increase in the rate of nitrosochlorination, whereas Ogloblin and Semenov established[44] that the reaction between nitrosyl chloride and methyl methacrylate is far more rapid in the presence of aluminium chloride. Further results are evidently required, which would enable the effect of Lewis acids on nitrosochlorination to be assessed with complete clarity. Perhaps such acids will be found to accelerate the reaction only in the case of alkenes having a certain structure, in particular those containing electron-acceptor groups.

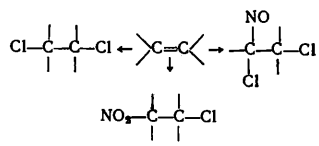
Ogloblin and Potekhin consider it possible that in several cases nitrosyl chloride adds by a nucleophilic mechanism:



Thus they showed[84] that $\alpha\beta$-unsaturated ketones form β-chloro-α-hydroxyimino-ketones very smoothly, in spite of the fact that the presence of a strongly electron-acceptor group adjacent to the double bond makes electrophilic addition difficult. Study of the reaction between nitrosyl chloride and $\alpha\beta$-unsaturated aldehydes also led the authors to the conclusion that such nucleophilic addition was possible. Thus under comparable conditions nitrosyl chloride reacts more vigorously with unsaturated aldehydes[31] than with the corresponding ketones[84]. A nucleophilic mechanism of nitrosochlorination is supported in this case by the effect of electron-donor substituents at the carbon–carbon double bond, which greatly lower the reaction velocity[31,84].

4. ANOMALOUS PRODUCTS OF NITROSOCHLORINATION

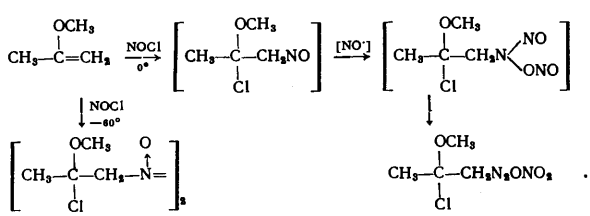
Although nitrosochlorination is widely used in synthetic practice for the preparation of chloro-nitroso- and chloro-hydroxyimino-compounds, it is nevertheless impossible in several cases to isolate the normal reaction products. The main side-processes are due to the chlorinating and oxidising action of nitrosyl chloride. The most generally occurring products of anomalous nitrosochlorination are dichlorides, dichloro-nitroso-compounds, and chloro-nitro-compounds, formed as follows:



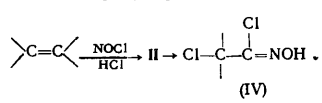
The factors determining the ratio of normal and anomalous nitrosochlorination products are extraordinarily diverse, and are often difficult to allow for exactly. Published data indicate that a substantial influence is exerted by the relative proportions of the reactants, the presence of acidic impurities in the nitrosyl chloride, the temperature of the reaction, and also the structure of the alkene. They indicate also that at elevated temperatures [33,48,81] nitration and chlorination will predominate over nitroso-chlorination.

Since in almost all cases the monomeric nitrosochlorides dimerise, Ogloblin et al. [50] explain the formation of dichloro- and nitro-chloro-derivatives in terms of the stability and the solubility of the dimeric nitrosochlorides. The formation of sparingly soluble and stable dimers would strongly diminish the yield of dichloro- and nitro-compounds; and conversely, good solubility of the dimers and ready dissociation into the monomeric forms will favour the appearance of anomalous nitrosochlorination products. These compounds are obtained by the interaction of nitrosyl chloride with the monomeric nitrosochloride of the alkene, taking place by a radical mechanism via unstable aliphatic diazo-nitrates [50].

Raising the temperature sometimes affects the formation of other reaction products in a definite manner. For example, reaction between nitrosyl chloride and 2-methoxypropene in ether at −60°C leads to formation of the nitrosochloride, whereas the same reaction at 10–15°C produces 2-chloro-2-methoxypropanediazo-nitrate, probably by a radical reaction with the monomeric nitrosochloride [30]:



As already mentioned above, in the presence of traces of hydrogen chloride the reaction of nitrosyl chloride with alkenes results in the formation of chloro-hydroxyimino-compounds [13–15,32,41]. However, cases have been observed in which chlorides of α-chlorinated hydroxamic acids can be obtained under these conditions [12–14,51,52]:



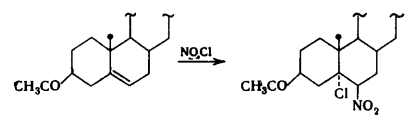
(IV)

The formation of dichloro-nitroso-compounds is obviously due to the chlorinating action of nitrosyl chloride. The interaction of oximes with this reagent results in geminal chloro-nitroso-compounds (IV) [112,113]. Therefore the formation of dichloro-nitroso-derivatives is facilitated preferentially if the reaction is conducted in the presence of excess of nitrosyl chloride. It is probable that the order in which the reactants are added plays a fundamental part in several cases.

In order that the nitrosochlorination of aliphatic alkenes should yield normal products, the double bond must have a certain nucleophilic character, and the reaction conditions must be maintained. Otherwise a complicated mixture of different addition products is formed.

In cases in which the addition of nitrosyl chloride to alkenes is difficult (i.e. in the presence of n-alk-1-enes and of alkenes containing electron-acceptor groups), the rates of chlorination and oxidation, leading to the formation of nitro-compounds, exceed the rate of addition of nitrosyl chloride, and the corresponding dichloro-compounds and chloro-nitro-compounds constitute the main products of the reaction [14,19,45,50–52,56,114–118].

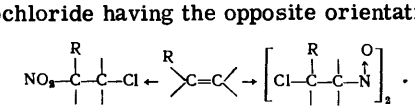
Cases are known in the literature in which chloro-nitro-compounds are formed extraordinarily readily, and are practically the sole products of the reaction [5–7]. For example, nitrosyl chloride reacts with cholesteryl acetate, the 3,17-diacetate of androst-5-ene, and 3-acetoxyandrost-5-en-17-one to form the corresponding 5-chloro-6-nitro-derivatives in high yield [5–7]:



The *trans*-diaxial positions of the chloro- and nitro-groups was established by a study of the reductive elimination of chlorine by the action of zinc dust in acetic acid [5], and also of the n.m.r. spectra [7].

Cholesteryl acetate reacts very slowly with pure nitrosyl chloride in ether at −5°C (a 53% yield of the nitrochloride was isolated after 2 months) [7]. It, however, unpurified nitrosyl chloride is used, the nitrochloride is formed quickly (in 92% yield after 5 days [5]). In the presence of nitrogen dioxide in ethereal solution the reaction is accelerated so much that the yield of the nitrochloride reaches 74% after only 2 h. This definitely indicates the possibility that this reaction is initiated by nitrogen dioxide, and in these cases the reaction probably consists in the free-radical *trans*-addition of nitryl chloride formed by the oxidation of nitrosyl chloride [12].

Such a mechanism is confirmed also by the fact that in several cases the chloro-nitro-compounds have an orientation of the nitro-group and the chlorine atom which is opposite to that to be expected for chloro-nitroso-compounds obeying Markovnikov's rule. Nevertheless, it should be noted that additions of nitryl chloride may show the opposite orientation to that observed in the reactions of nitrosyl chloride. Thus the nitrosochloride of an alkene is not the precursor of the nitrochloride of the alkene. For example, Yakubovich and Lemke [72] showed that the reaction of nitrosyl chloride with 2-methylpropene gives, together with the nitrosochloride, a small quantity of the nitrochloride having the opposite orientation:



A similar course of reaction, leading to the nitrochloride as the sole product, has been noted also by Andrianov et al.[119] in the case of 3-vinylheptamethylsiloxane:

$$2\,(CH_3)_3SiOSi(CH_3)OSi(CH_3)_3 + 2NOCl \rightarrow N_2 + Cl_2 + 2\,(CH_3)_3SiOSi(CH_3)OSi(CH_3)_3$$
$$\quad\quad\quad

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The Chemistry of Azaindoles [Pyrrolo[2,3]pyridines†]

L.N.Yakhontov

The review discusses the chemical properties and the biological activity of aza-analogues of indole compounds, i.e. substances containing fused pyridine and pyrrole systems.
The interest taken in azaindole derivatives is due on the one hand to the ever broadening application during recent years of the principle of building up aza-analogues of biologically active substances (purines, pyrimidines, steroids, etc.) as bases in the search for new medicinal preparations, and on the other hand to the appearance in such systems of characteristic chemical properties, indicating a redistribution of electron density caused by the interaction of the "π-electron-deficient" and "π-electron-excessive" rings involved in the fusion.
The above problems are fully reflected in the review. Considerable attention is paid to discussing the chemical peculiarities of azaindoles associated with the presence in the fused systems of rings which have directly opposite displacements of π-electrons relative to carbon atoms, describing the features of lactam-lactim and amino-imino tautomerism in azaindole and azaindoline systems, and also examining routes and methods for introducing substituents both into the pyridine and into the pyrrole parts of the molecule. Exhaustive consideration is given to data on the biological activity of azaindoles. A special section is concerned with the choice of methods for building up azaindole systems and the characteristics of ring-closure in azaindoles compared with indoles.
The review covers all information available in the world's literature on the chemistry and the biological activity of azaindoles. The list of references comprises 159 items.

CONTENTS

I.	Introduction	551
II.	Methods of preparing azaindoles	552
III.	Chemical properties of azaindoles	558
IV.	Biological activity of azaindole compounds	563

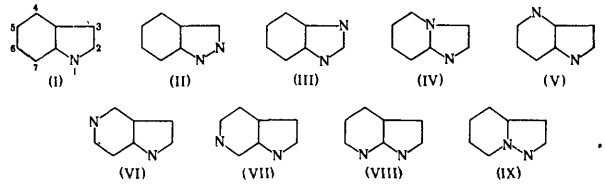
I. INTRODUCTION

In recent years the search for new medicinal preparations has been based with increasing frequency on the possible similarity or antagonism of the pharmacological action of biologically important compounds and their aza-analogues, substances in which one or more carbon atoms have been replaced by nitrogen.

Investigation of aza-analogues of pyrimidine and purine bases has enabled substances exhibiting considerable tumorstatic activity[6,7] to be obtained in the series of azaguanines[1], azauracils[2,3], azacytosines[4], and azathymines[5]. It has been established that aza-analogues of purine and pyrimidine bases, subjected in the organism to the processes of ribosidation and phosphorylation, become powerful inhibitors of several successive steps in the biosynthesis of pyrimidine nucleotides. Thus 6-azacytosine is converted in the tumour cells of Ehrlich's ascitic cancer into 6-azacytidine 5'-phosphate, which is an orotidylic acid decarboxylase inhibitor[4]. An analogous enzymic conversion product of 6-azauracil—6-azauridine monophosphate—blocks orotic acid decarboxylase, and interferes with the synthesis of uridylic acid[8,9].

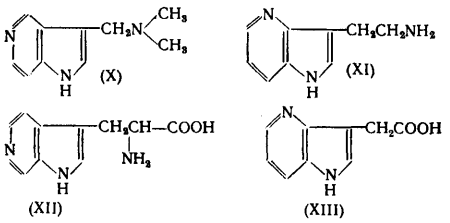
Study of the aza-analogues of steroid hormones[10-16] has brought to light compounds of interest not only from the point of view of their hormonal activity. This makes understandable the interest shown by chemists and biologists in the investigation of azaindoles, the simplest aza-analogues of the physiologically important indole compounds.

All products in which one of the carbon atoms of the indole ring (I) has been replaced by nitrogen are formally azaindoles. However, such a broad interpretation, adopted by several authors[17], includes in this class substances which are extremely diverse in chemical properties—pyrrolopyridines (V)–(VIII), benzimidazoles (III), indazoles (II), pyrimidazoles (IV), and pyrazolopyrimidines (IX):

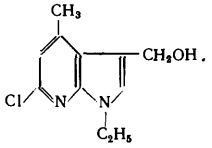


It appears advisable to restrict the concept of "azaindoles" by retaining this name only for products in which one of the atoms not common to the two rings in the indole molecule has been replaced by nitrogen (V)–(VIII), without, in contrast to Adler and Albert[18-20], regarding benzimidazole (III) and indazole (II) as azaindoles.

The nomenclature of the azaindoles is based on the principles used in constructing the names of indole compounds. The most widely used is addition of the position of the aza-substituent to the name of the corresponding indole derivative—4-azaindole (V), 5-azaindole (VI), 6-azaindole (VII), 7-azaindole (VIII), 5-azagramine (X), 4-azatryptamine (XI), 6-azatryptophan (XII), 4-azaindol-3-ylacetic acid (XIII), 6-chloro-1-ethyl-4-methyl-7-azaindol-3-ylmethanol (XIV), etc.:



† Although the "aza" system of nomenclature should strictly be based on the corresponding homocyclic compounds, the Reviewer's nomenclature has been followed in the Translation, especially as he discusses his choice of nomenclature in the Introduction (Ed. of Translation).

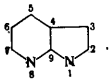


(XIV)

This most widely used principle of nomenclature is adopted in the present review.

It should be noted, however, that other terms of azaindole compounds are met in the literature. Azaindoles are most often named as diaza-analogues of indane[21-23], e.g. 1,4-diazaindane (V), 1,6-diazaindane (VII), etc. In American journals azaindoles are not infrequently considered to be derivatives of pyrrolopyridines[24-27], e.g. 1*H*-pyrrolo[2,3-*b*]pyridine (VIII), 1*H*-pyrrolo[3,2-*c*]pyridine (VI), etc.‡. An analogous nomenclature is found also in German papers[28], e.g. pyrrolo(2,3 : 2'3')pyridine (VIII).

In earlier papers azaindoles were termed pyrindoles[29,30]. Besides the above numbering of the rings, e.g. 7-pyrindole (VIII)[29], another system was also used, according to which the compound (VIII) was termed 8-pyrindole[31]:



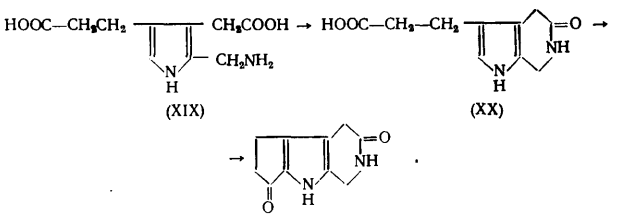
Quite often trivial names are used—harmyrine for 6-azaindole, and apoharmine for its 7-methyl derivative—reflecting the historical relation between 6-azaindoles and the harmine group of alkaloids.

II. METHODS OF PREPARING AZAINDOLES

1. Naturally Occurring Azaindoles

Most azaindole derivatives are synthetic products. The only naturally occurring unsubstituted azaindole which has yet been found is 7-azaindole, discovered in 1943 by Kruber[28] in the lepidine fraction of coal-tar. Nevertheless, the bicyclic 6-azaindole system is widely distributed as part of the fused polycyclic structures of various groups of alkaloids—yohimbine, canthine, harmine, corynanthine—alstonine, sarpagine–ajmaline, etc. Since such fused systems are not discussed in the present paper, we merely mention them, referring readers who are interested to specialised reviews on the chemistry of the alkaloids[32-35].

Derivatives of 6-azaindole are of definite value also in the chemistry of porphobilinogen (XIX), an intermediate in the biosynthesis of porphyrins[36]. A key compound in the study of the structure of porphobilinogen[37-39] was its lactam (XX)[40], a derivative of tetrahydro-oxo-6-azaindole. Conversion of porphobilinogen (XIX) into the lactam (XX) followed by closure of the five-membered ketone ring enabled the position and the nature of the side-chains in (XIX) to be determined[40]:



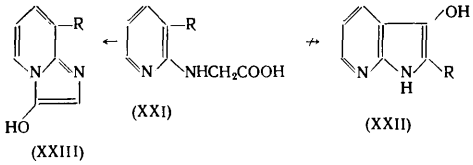
(XIX) (XX)

‡ The preceding examples in this paragraph are consistent with the recommendations of the International Union of Pure and Applied Chemistry (Ed. of Translation).

2. Features of the Synthesis of Azaindole Systems

Synthetic investigations in the azaindole series began in connection with the modification of indigoid dyes, when the idea arose of synthesising pyridine analogues of indigo, and publications appeared on a "new class of indigoid dyes", which were "pyrindole" derivatives. The key reaction in these syntheses was the cyclisation of substituted pyrid-2-ylaminoacetic acids (XXI) into the corresponding 7-azaindoxyls[41,42].

However, further research showed[43-45] that the course of this reaction in the pyridine series was different from that found in benzene derivatives. Ideas on the structure of the bicyclic pyridine product, based solely on analogies with indole derivatives, proved to be erroneous. Actually, cyclisation of the substituted pyrid-2-ylaminoacetic acids (XXI) led to the formation not of 7-azaindoxyls (XXII) but of compounds of the pyrimidazole series (XXIII):

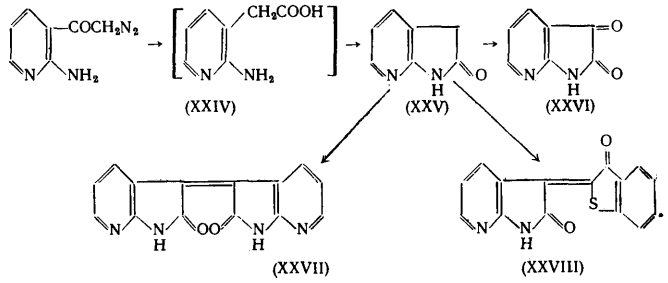


(XXIII) (XXI) (XXII)

where R = H, COOH.

Nor did subsequent work on the cyclisation of 4-carboxymethylamino-2,6-dimethylpyridine-3-carboxylic acid lead to azaindigoid dyes[46].

It was only in 1941 that Kägi[29] was able to obtain 7-azaoxindole (XXV) by the cyclisation of 2-aminopyrid-3-ylacetic acid (XXIV) and accomplish the conversion of (XXV) into 7-azaisatin (XXVI) and 7-azaindigoid vat dyes (XXVII) and (XXVIII). These researches have been further developed by the synthesis of 4-, 5-, and 6-azaindigos[47]:



(XXIV) (XXV) (XXVI) (XXVII) (XXVIII)

The initial failures to synthesise azaindigoid dyes were not fortuitous, and are of considerable interest for the chemistry of the azaindoles. In contrast to compounds of the benzene series, in which electrophilic substitutions occur comparatively readily, analogous reactions are accomplished with great difficulty in the pyridine ring, where the electron-acceptor properties of the cyclic nitrogen atom diminish the electron density on the carbon atoms. Furthermore, pyridine derivatives contain a ring nitrogen enriched with electrons, which easily acts as a nucleophilic centre in an addition reaction, and in the case of 2-aminopyridine derivatives also in nucleophilic substitution (with migration of the reaction centre).

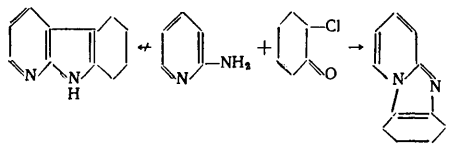
The peculiarities in the closing of azaindole compared with indole rings are due to these two factors—the lower electron density on the ring carbon atoms and the presence of a heteroatom having increased electron density.

The above method for obtaining indoxyls, and also the numerous reactions (Fischer, Harley-Mason, Reissert, Bischler–Napieralski, Pictet, Pomeranz–Fritsch reactions, etc.), which are widely used for synthesising various

heterocyclic systems from benzene derivatives, necessarily pass through a stage of electrophilic substitution in the benzene ring.

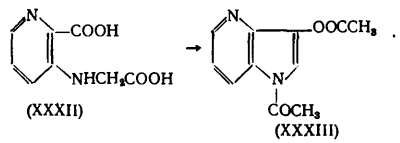
An analogous electrophilic substitution at a carbon atom is always more difficult and requires severe conditions on passing to the corresponding pyridine derivatives[48]. Furthermore, the competing process at the pyridine nitrogen becomes in several cases the main reaction, and prevents the use for preparing azaindoles of synthetic methods which have been widely and successfully employed in the chemistry of indole compounds.

Disregard of the peculiarities of the pyridine molecule in comparison with the benzene molecule led to errors not only in studying the cyclisation of pyrid-2-ylaminoacetic acid but also in several other cases. For example, a patent was applied for[49] in 1930 claiming the preparation of 9,10,11,12-tetrahydro-α-carboline (XXIX) by the reaction of 2-aminopyridine (XXX) with 2-chlorocyclohexanone. Later workers have shown[50] that the product of this reaction is not (XXIX) but 6,7,8,9-tetrahydropyrido[1,2-a]-benzimidazole (XXXI):



(XXIX) (XXX) (XXXI)

Thus in this case the reaction follows the general path of interaction between α-halogeno-carbonyl compounds and 2-aminopyridine discovered by Chichibabin[51]. A pyrimidazole derivative was probably formed also in the cyclisation of 2-carboxymethylaminopyridine-3-carboxylic acid described by Willette[52]. The analogous process of cyclisation of 2-carboxypyrid-3-ylaminoacetic acid (XXXII) yielded 1-acetyl-4-azaindol-3-yl acetate (XXXIII)[52]:



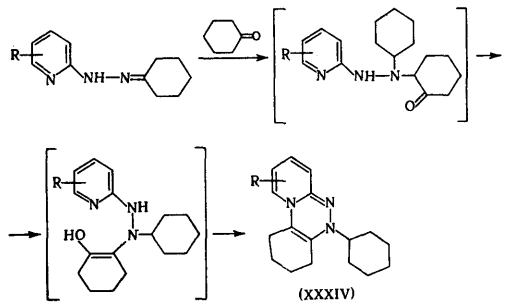
(XXXII) (XXXIII)

3. Application of the Fischer Reaction

The peculiar features of the chemical behaviour of pyridine compounds noted above have been responsible for the restricted application in the azaindole series of one of the most general methods for synthesising various indole compounds, the Fischer reaction. While going easily and smoothly with various arylhydrazones[53-55], this reaction does not usually give positive results with pyridyl- and quinolyl-hydrazones[21,22,56-60]. Successful synthesis of azaindoles by the Fischer method could be accomplished only from the pyridylhydrazones of a few ketones—cyclohexanone[58-60], 3-methylbutan-2-one[21,22], desoxybenzoin[60,61], cyclopentanone[62], indan-1-one[62], and α-tetralone[62].

A study of condensing agents has shown that in all cases considerably more severe conditions are required for the cyclisation of pyrid-2-ylhydrazones than for that of the corresponding arylhydrazones[63]. For example, catalytic quantities of zinc chloride or copper(I) chloride, which with cyclohexanone phenylhydrazone ensure that the Fischer reaction shall occur normally from 180°C,[64,65] enable only the original compound to be isolated in the case of the pyrid-2-ylhydrazone even at 240°C.[66] The Fischer cyclisation of pyrid-2-ylhydrazones is difficult even when boron trifluoride is used as catalyst. Only the application of strong mineral and arenesulphonic acids has made it possible to accomplish the conversion of cyclohexanone pyrid-2-ylhydrazones into 5,6,7,8-tetrahydro-α-carbolines in yields up to 98%.[67] Electron-donor substituents in the 5- and 6-positions of the pyridine ring, by increasing the electron density on the third carbon atom, facilitate the reaction, whereas electron-acceptor substituents hinder the process[66].

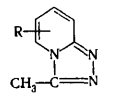
Nevertheless, it has been shown[63] that the cyclisation of cyclohexanone pyrid-2-ylhydrazones in the presence of hydrochloric acid, and also with an acetic-acid solution of the boron trifluoride–ether complex, involves "anomalous" reactions caused by the nucleophilic character of the nitrogen of the pyridine ring. The "anomalous" products of cyclisation in hydrochloric acid which have been isolated[63] are 9-cyclohexyl-5,6,7,8,9,12-hexahydro-9,10,12-triazaphenanthrene derivatives (XXXIV), the mechanism of whose formation can be written



(XXXIV)

In strongly acid medium the initial hydrazone is partly hydrolysed with the formation of cyclohexanone, which, by means of the reactive methylene group, adds at the C=N bond of the hydrazone. Subsequent enolisation of the ketone and elimination of water are facilitated by formation of the energetically favourable dihydro-1,2,10-triazanaphthalene system. Such a mechanism for the process is supported by the fact that the yield of (XXXIV) is more than trebled by the addition of an equimolecular quantity of cyclohexanone to the reaction mixture.

The "anomalous" course of the Fischer reaction in an acetic-acid solution of the boron trifluoride–ether complex is also due to acid hydrolysis. The pyrid-2-ylhydrazines which are thus obtained are acylated by the acetic acid, with further cyclisation of the acetyl derivatives into 3-methyl-1,2,9-triazaindenes (XXXV)[66]:

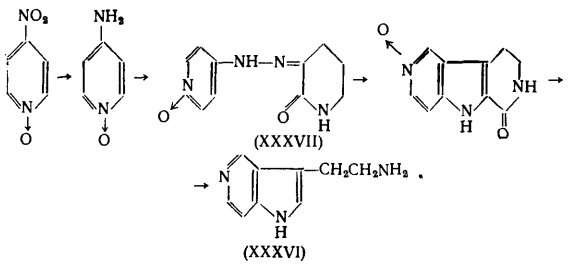


(XXXV)

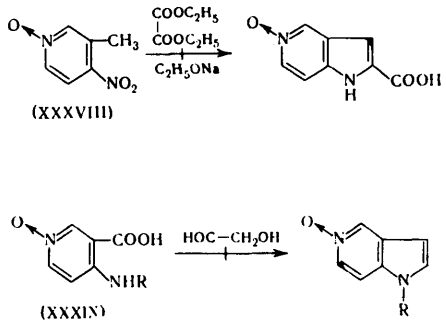
The above "anomalous" reactions are general in character, and are repeated with various substituted pyrid-2-ylhydrazones of cyclohexanone (R = H, 5-CH_3, 6-CH_3, 5-Cl, 5-Br, etc.)[66,67].

Since it has been established that the cyclisation of pyrid-2-ylhydrazones can be influenced by introducing substituents into the pyridine ring[66], it is worth looking into the Fischer synthesis of azaindoles from 6-chloropyrid-3-ylhydrazones of acetone and propionaldehyde[68], and also the successful application of the scheme of Abramovich and Shapiro for preparing 5-azatryptamine (XXXVI) from

the $N_{(1')}$-oxide of 2,3-dioxopiperidine 3-pyrid-4'-yl-hydrazone (XXXVII)[69]:



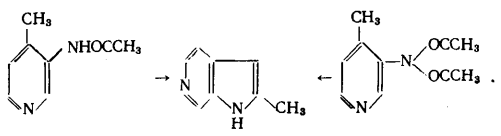
These results are especially interesting because attempts to synthesise 5-azaindole derivatives from the *N*-oxide of 3-methyl-4-nitropyridine (XXXVIII) by the Reissert reaction and from the $N_{(1')}$-oxide of 4-methyl(or phenyl)aminonicotinic acid (XXXIX) by the Harley-Mason reaction were unsuccessful[70]:



where R = CH_3, C_6H_5.

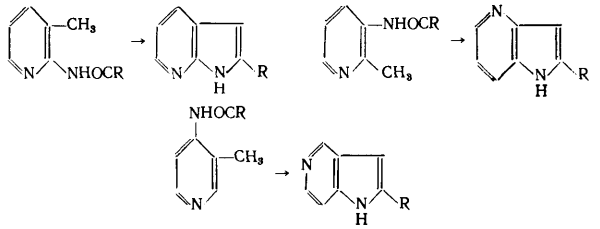
4. Application of the Madelung Reaction

Among methods which are widely used in the chemistry of indole, the Madelung synthesis[71] has found the widest application for the preparation of azaindole compounds. In 1927 Koenigs and Fulde[30] used this reaction to prepare the first synthetic azaindole derivative, 2-methyl-6-azaindole, a yield of 23% being obtained by the cyclisation of 3-acetamido-4-methylpyridine in the presence of sodium ethoxide. Somewhat better yields (up to 40%) were achieved from the corresponding 3-diacetylamino-4-picoline[25]:



It has proved impossible to convert the corresponding 3-formamido-derivative into unsubstituted 6-azaindole[30]. In all other cases formamidopyridines are poorer starting materials for azaindoles than are aminopyridines acylated by other acids.

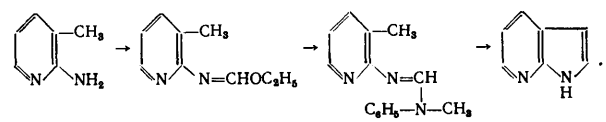
The Madelung method was later used for the synthesis of 4-, 5-, and 7-azaindole derivatives[72,73]:



The best results (yield 20%) were obtained in the case of 4-azaindole, while the yield of 7-azaindole was 3%, and unsubstituted 5-azaindole could not be synthesised by this method. The cyclisation of 4-acetamido-3-picoline to 2-methyl-5-azaindole took place with a yield of only ~ 1%. The same method enabled 5-methyl-4-azaindole (yield 12%) to be synthesised from 3-acetamido-2,6-lutidines, as well as the corresponding 2-methyl and 2-phenyl derivatives (yields 55% and 67% respectively)[23,74], while from 3-acylamino-4-picolines 12–24% yields were obtained of 2-phenyl-, 2-pyrid-2'-yl-, and 2-pyrid-4'-yl-6-azaindoles[75].

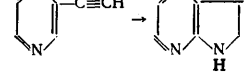
Further improvement of the Madelung reaction involved the use of sodium anilide and potassium formate as condensing agents[76], which enabled the yield of 7-azaindole at the cyclisation stage to be increased to 51%.[77] Rather lower yields (13–38%) are obtained for 4-, 5-, and 6-methyl-7-azaindoles[78]. Unfortunately, this modification of the Madelung reaction did not give favourable results for the 5- and 6-azaindoles. Conversion of 4-formamido-3-picoline in the presence of sodium anilide into a 21% yield of 5-azaindole[79] could not subsequently be repeated[24,25]. Published data[20,25] on the possibility of obtaining 4-azaindole by this method are also contradictory.

An interesting modification of the Madelung method was described in 1965 by a group of American workers[80], who showed that the best results are obtained by cyclising not formamidopicolines but the corresponding formamidine derivatives:



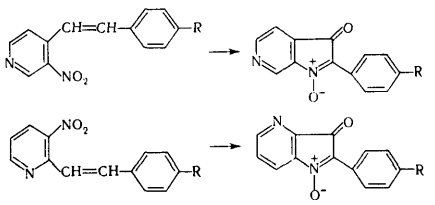
This procedure gives yields, based on the initial aminopicolines, of 70%, 37%, and 6% respectively of 7-, 5-, and 4-azaindoles.

It is worth noting the synthesis, recently published by Reisch[81,82], of unsubstituted 7-azaindole from 3-ethynylpyridine and sodamide, the yield being 54%:



The 2-amino-3-ethynylpyridine formed by the Chichibabin reaction in the course of the synthesis is immediately cyclised to 7-azaindole. A fundamental defect of this method is the relative inaccessibility of the initial 3-ethynylpyridines[83–85]. As Kost et al.[85] have shown, the preparation of 3-ethylnylpyridines from 3-vinylpyridines via the dihalogeno-derivatives is usually accompanied by the formation of 3-1'-alkoxyvinylpyridines as a side-reaction. In some cases the production of acetylenic derivatives of the pyridine series is so unsatisfactory that the method of synthesis via 3-ethynylpyridines loses its practical value.

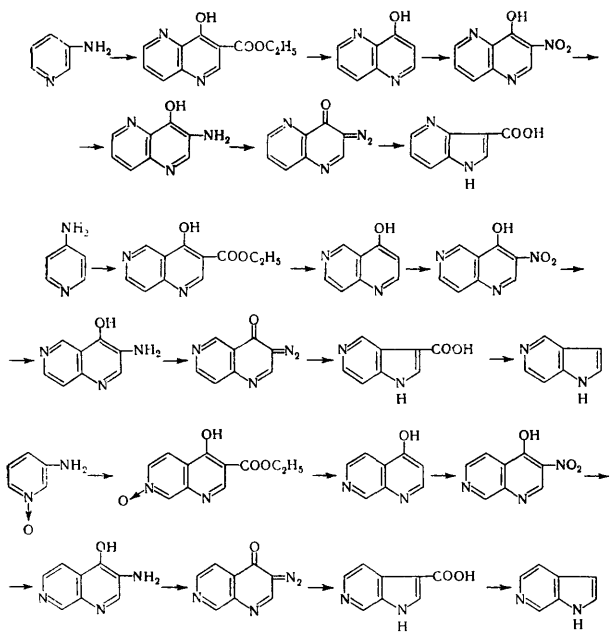
For example, Hooper et al.[75] intended to synthesise 1-hydroxy-3-oxo-4(and 6)-azaindolines from 3-nitro-2-(and 4)-styrylpyridines via the corresponding phenylethynyl derivatives. However, failures in obtaining the initial ethynyl compounds forced them to reject this scheme. The use of Splitter and Calvin's method[86] in this case enabled 2-aryl-1-hydroxy-3-oxo-4(and 6)-azaindolines to be obtained by the ultraviolet irradiation of substituted 3-nitro-2(and 4)-styrylpyridines[75]:

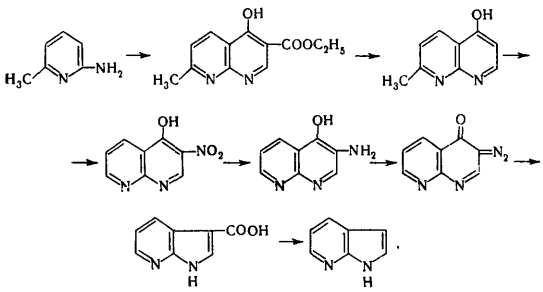


where R = $N(CH_3)_2$, OH.

5. Synthesis of Azaindoles by Süs and Möller's Method

An original photochemical method for preparing azaindoles from 3-diazo-3,4-dihydro-4-oxonaphthyridine isomers was described by Süs and Möller[87-89]. The starting materials used for the preparation of 4- and 5-azaindoles were respectively 3- and 4-aminopyridines, which were converted into 4-hydroxynaphthyridine-3-carboxylic esters by condensation with ethoxymethylenemalonic ester[90]. Subsequent stages consisted in saponification of the ester, decarboxylation, nitration, reduction of the nitro-group, and diazotisation of the 3-amino-4-hydroxynaphthyridines[87-89]. In the case of 6-azaindoles[88] the starting material for the preparation of 1,7-naphthyridine derivatives had to be 3-aminopyridine *N*-oxide, since unoxidised 3-aminopyridine could be converted only into substituted 1,5-naphthyridine[91]. In the preparation of 7-azaindole[89] 2-amino-6-methylpyridine was treated with ethoxymethylenemalonic ester; 2-aminopyridine which is not substituted in the 6-position forms in this case a pyrido[1,2-*a*]pyrimidine derivative, owing to cyclisation of the pyridine ring at the nitrogen atom[91]:



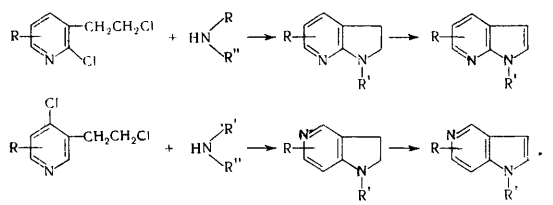


Photochemical ring contraction in the 3-diazo-3,4-dihydro-4-oxo-derivatives of the isomeric 1,5-, 1,6-, 1,7-, and 1,8-naphthyridines yields respectively the 4-, 5-, 6-, and 7-azaindole-3-carboxylic acids. With the exception of 4-azaindole-3-carboxylic acid, these are readily decarboxylated to isomeric azaindoles[87-89].

In spite of the multistage character of the process, it has proved valuable in the preparation of unsubstituted azaindoles. However, the comparatively severe reaction conditions restrict its use for obtaining azaindoles containing functional substituents.

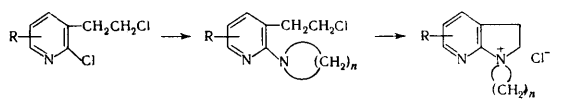
6. Syntheses of Azaindolines from 2(and 4)-Chloro-3-2'-chloroethylpyridines

A general method for synthesising various derivatives of 5- and 7-azaindoles[66,92-101] is to treat 3-2'-chloroethylpyridines containing halogen in position 2 or 4 with ammonia or a primary or secondary amine. The resulting azaindolines lose two hydrogen atoms on dehydrogenation, and are converted into the substituted azaindoles:



The reaction between 2(or 4)-chloro-3-2'-chloroethylpyridine and a secondary amine involves a novel type of pyrroline ring-closure accompanied by *N*-dealkylation. The reaction begins with replacement of the 2(or 4)-chlorine atom by the radical of the secondary amine, which is followed by cyclisation with formation of a quaternary azaindolinium salt, and this splits off alkyl halide, being thereby converted into a 1-alkyl(or aryl)-7-azaindoline.

The use of cyclic secondary amines (piperidine and pyrrolidine), by breaking up the process, permitted observation of the two successive stages—replacement of chlorine in the 2-position of the pyridine ring by the residue of the secondary amine, and subsequent cyclisation with the formation of spiro-7-azaindolinium compounds[102]—the reactions terminating at the latter stage, since in this case the quaternary 7-azaindolinium salt is unable to split off alkyl halide:



where n = 4, 5.

Study of the factors governing the ease of formation of 7-azaindoline derivatives by the above procedure indicates that the first stage of the reaction—replacement of the chlorine atom in the pyridine ring by the residue of the

secondary amine—is fundamentally influenced by the reactivity of the attacking nucleophilic agent, the lability of the halogen under attack, and also the competition of side-reactions. A decisive factor in the concluding stage of the synthesis is the ease of rupture of the carbon–nitrogen bonds in the quaternary azaindolinium derivative.

If steric factors are disregarded, increasing the basic strength of the secondary amine facilitates reaction with 2-chloro-3-2′-chloroethylpyridines and the formation of 7-azaindoline derivatives; secondary processes are facilitated at the same time. Thus, for example, *N*-substituted anilines ($pK_a < 6$) react with 2,6-dichloro-3-2′-chloroethyl-4-methylpyridine (trichlorocollidine) only at 190°C,[92,94] whereas aliphatic secondary amines ($pK_a > 9$) react similarly at only 80–140°C.[92] Nevertheless, 1-arylazaindolines are obtained from reactions with *N*-substituted anilines invariably in high yields, sometimes close to theoretical. The presence of electron-acceptor substituents in the *para*-position of *N*-alkylanilines hinders the reaction, whereas electron-donor groups facilitate the process[97].

When aliphatic secondary amines are used, formation of azaindolines is accompanied by that of secondary products[92,103], primarily derivatives of 2-chloro-3-vinylpyridine. Raising the temperature accelerates both processes—replacement of the 2-chlorine by the radical of the amine, which increases the yield of azaindoline derivative, and elimination of hydrogen chloride from the side-chain, which shifts the reaction towards the 2-chloro-3-vinylpyridine—the rate of the second process increasing more rapidly than that of the first with rise in temperature.

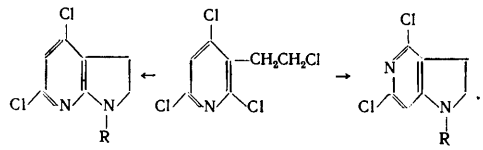
In the case of diphenylamine interaction with trichlorocollidine begins only at 300°C, the product being not an azaindoline derivative but 2-chloro-6-diphenylamino-4-methyl-3-vinylpyridine[92]. This course of the reaction is due not only to the low basic strength of the aromatic secondary amine (pK_a 0.9) but also to steric hindrance. The influence of steric factors appears also in other cases of reaction between 2-chloro-3-2′-chloroethylpyridines and secondary amines. For example, the ease of formation of azaindolines varies inversely with the length of the alkyl chain in the secondary amine[92]. Reactions with homologous dialkylamines or *N*-alkylanilines at the same temperatures reveal an increase in the yield of azaindoline derivatives as the alkyl chain becomes shorter[92,94].

The question of the relative reactivity of different electrophilic centres in substituted 2-chloro-3-2′-chloroethylpyridines towards amines has been examined most generally in the case of 2,6-dichloro-3-2′-chloroethyl-4-methylpyridine (trichlorocollidine), study of whose reactions with various nucleophilic agents has shown[104] that the chlorine in the side-chain of this compound is easily eliminated as hydrogen chloride and is very resistant to nucleophilic substitution.

Of the two ring chlorine atoms, that in position 2 is the more mobile, while nucleophilic attack at position 6 plays no important part, except where reaction at position 2 is sterically hindered[103]. As a consequence, only 1-substituted 6-chloro-7-azaindolines are formed at temperatures up to 270°C with various secondary aliphatic and aliphatic–aromatic amines, as also with *N*-alkyl(and aralkyl)anilines. The chlorine atom in position 6 is retained even in the presence of large excesses of secondary amines.

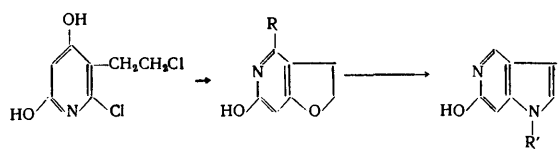
Further rise in temperature levels off the difference in reactivity between the halogen atoms in positions 1 and 6. At 300°C, for example, trichlorocollidine and *N*-methylaniline form no longer 6-chloro-4-methyl-1-phenyl-7-azaindoline but 4-methyl-1-phenyl-6-phenylamino-7-azaindoline[94]. It is interesting that in this case the *N*-dealkylation involved in closure of the pyrroline ring is accompanied by *N*-dealkylation of the 6-substituent. Since the product of the reaction of 6-chloro-4-methyl-1-phenyl-7-azaindoline with *N*-methylaniline, also occurring at 300°C, is 4-methyl-6-*N*-methyl-*N*-phenylamino-1-phenyl-7-azaindoline, not the corresponding *N*-desmethyl derivative, it can be assumed that replacement of the 6-chlorine by the amine residue in the high-temperature reaction of trichlorocollidine with *N*-methylaniline takes place either before or during, but not after, closure of the pyrroline ring[94].

The synthesis of azaindolines is considerably influenced by substituents in the initial 2-chloro-3-2′-chloroethylpyridines, which produce definite quantitative and in several cases even qualitative differences in the course of the reaction[66,92,93,97,98]. 2,4,6-Trichloro-3-2′-chloroethylpyridine undergoes two competing reactions with amines, with the formation of 5- and 7-azaindolines[96]:



The use of 2,4-dichloro-5-2′-chloroethylpyridine opened up the possibility of the directed synthesis of 5-azaindoline derivatives[66].

Dehydrohalogenation with closure of a dihydrofuran ring takes place extraordinarily easily in the case of 2-chloro-3-2′-chloroethyl-4,6-dihydroxypyridine, which opens new routes to the preparation of the hitherto difficultly accessible bicyclic 1-oxa-5-azaindane system[66]. Derivatives of this system on treatment with amines are readily converted into the corresponding 5-azaindoles[66]:



where R = Cl, H.

Further study of ways of synthesising azaindoline derivatives showed that not only 2-chloro-3-2′-chloroethylpyridines but also the corresponding 2-chloro-3-2′-hydroxyethyl and 2-chloro-3-2′-methoxyethyl-pyridines could react with secondary amines[105]. In this case, however, azaindoline derivatives could be synthesised only at higher temperatures (300–350°C). The mechanism of the formation of azaindolines from these 3-2′-hydroxy- and 3-2′-methoxy-ethylpyridines is probably analogous to that obtaining in the case of the 2-chloro-3-2′-chloroethylpyridines. The differences in reaction conditions are probably connected with the influence of the substituents in the side-chain (methoxy, hydroxy, chloro) on the lability of the 2-halogen atom. Transmission of the inductive effect of substituents through a chain of two carbon atoms and a pyridine ring can be observed also in other cases[105].

The final stage in the formation of 1-substituted 7-azaindolines from 2-chloro-3-2′-chloroethylpyridines and secondary amines is dealkylation of the quaternary azaindoline derivative. In the case of symmetrical secondary amines *N*-dealkylation is practically unambiguous: detachment of the alkyl (aralkyl) group is energetically more favourable than cleavage of the pyrroline ring. With unsymmetrical secondary amines which carbon–nitrogen bond undergoes cleavage in the quaternary azaindolinium

derivative is determined by the relative strengths of the bonds linking the substituents to the nitrogen atom: benzyl groups are more readily detached than are alkyl groups, and the latter considerably more easily than aryl groups[66].

The alkyl (or aralkyl) chloride which is eliminated in the process of dealkylation reacts under the given conditions with excess of the secondary amine, converting it into a tertiary amine. The corresponding tertiary amines have been detected and determined quantitatively by gas–liquid chromatography, after which samples were isolated[66].

7. Dehydrogenation of Azaindolines

Various methods of dehydrogenation have been used to convert azaindolines into the corresponding azaindoles. In the case of 1-alkyl(aryl)-7-azaindolines the most general method proved to be boiling with chloranil in xylene[93-97]. In most cases the reactions go smoothly with yields of 45–91%.

Dehydrogenation is facilitated by the presence of a 6-methoxy-group in the azaindoline molecule. With 4,6-dichloro- and 1-aryl-6-chloro-7-azaindolines, on the other hand, the oxidising potential of chloranil is inadequate, and a stronger oxidant, 2,3-dichloro-5,6-dicyanobenzoquinone, is required to convert such compounds into the azaindoles[96].

The process of dehydrogenation is considerably affected by the nature of the substituent attached to the pyrroline nitrogen. The introduction of an electron-acceptor substituent into position 1 of the azaindoline molecule hinders dehydrogenation, while the process is facilitated by an electron-donor substituent[66]. In the case of such strong electron-acceptor residues as acyl groups, dehydrogenation takes place neither on boiling with chloranil in xylene nor on heating with sulphur or with selenium to 240–300°C.[95]

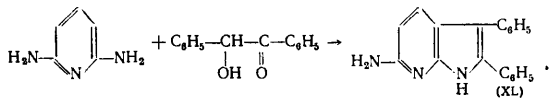
On passing from indolines and azaindolines to their *N*-sodio-derivatives (more accurately anions), when the electron density on the pyrroline nitrogen is greatly increased, the reduction potentials of the compounds rise markedly, and even air is a sufficiently strong oxidant to convert these substances into the corresponding indoles and azaindoles[106]. The dehydrogenation of indolines and azaindolines is accomplished in this case by treating their solutions in liquid ammonia with sodium in the presence of air. Separate experiments have shown that dehydrogenation does not take place in the absence of atmospheric oxygen[107].

Other strong bases—sodium hydride, sodamide, caustic soda—can be used instead of sodium. The yield of dehydrogenation products then varies directly with the strength of the base: with sodium hydride the extent of the process is about 80–85%, roughly the same as with metallic sodium, with sodamide 50–55%, with caustic soda 30–35%, and with sodium carbonate only traces of dehydrogenation products are formed[107]. Liquid ammonia is a convenient solvent for this reaction, and although the process goes also when indolines and azaindolines are treated with sodium in boiling toluene, formation of the corresponding anions is difficult under the conditions of a heterogeneous reaction, and the yields of dehydrogenation products are diminished.

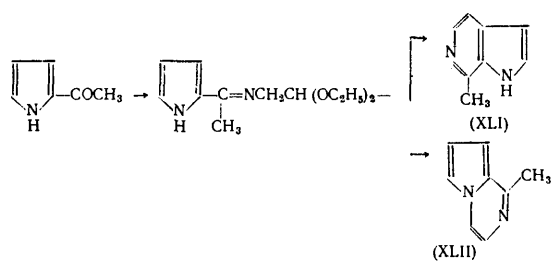
The possibility of combining into one stage, by the method which has been developed, the dehydrogenation of azaindoline derivatives with dehalogenation, and also the elimination of *N*-acyl and *N*-benzyl protective groups, is of considerable preparative interest[106].

8. Other Methods of Synthesising Azaindoles

Apart from the more or less general methods for obtaining azaindoles described above, syntheses have been published which are applicable only to individual compounds of this type. For example, formation of 6-amino-2,3-diphenyl-7-azaindole (XL) in 89% yield was observed on the reaction of 2,6-diaminopyridine and its hydrochloride with benzoin[26]. Unfortunately, this example proved to be unique, and in no case could azaindole compounds be isolated by the reaction of 2,6-diaminopyridine with other hydroxy-ketones:



Apoharmine (XLI) was synthesised[108,109] from 2-acetylpyrrole by the Pomeranz–Fritsch reaction:

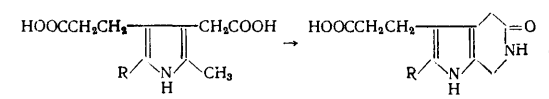


However, cyclisation of the 2-*N*-(2,2-diethoxyethyl)acetimidoylpyrrole went unexpectedly: together with (XLI), the stable yield of which did not exceed 5%, the formation was observed of a substituted 5,8-diazaindene (XLII). In the analogous synthesis from the corresponding 2-formidoyl derivative, the pyrrolopyrazine derivative was practically the only product of the reaction.

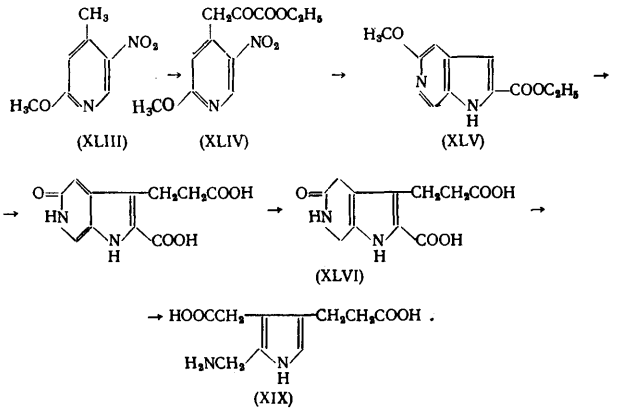
Low yields (1–7%) of 7-azaindole derivatives were obtained, accompanied by other compounds, by Johnson and his coworkers by treating diethyl 4-cyano-4,5-dihydro-2,7-dimethylazepine-3,6-dicarboxylate with silver nitrate[110] and by the reaction of potassium cyanide with dimethyl 4-chloromethyl-1,4-dihydro-1,2,6-trimethylpyridine-3,5-dicarboxylate[111].

The cyclisation of amino-carboxylic acids of the pyridine or pyrrole series to the corresponding lactams has occupied a definite place in the synthesis of azaindoles. As noted above, 7-azaoxindole was prepared from 2-aminopyrid-3-ylacetic acid by this method[29]. However, the poor accessibility of other aminopyridylacetic acids has not permitted the isomeric 4-, 5-, and 6-azaoxindoles to be synthesised[24,60].

3-Carboxyethyl-4-carboxymethyl-5-methylpyrroles, both substituted and unsubstituted in position 2, were used as starting materials in the synthesis of lactams of porphobilinogen and its analogues[112-115]. The 5-methyl group in these compounds was converted into aminomethyl either via the aldehyde, oxime, and nitrile[113,114] or via bromomethyl. Cyclisation of the substituted 5-aminomethyl-4-carboxymethylpyrroles was brought about by heating in acetic anhydride. The products of the synthesis were various 2-substituted 4,5,6,7-tetrahydro-5-oxo-6-azaindol-3-ylpropionic acids:

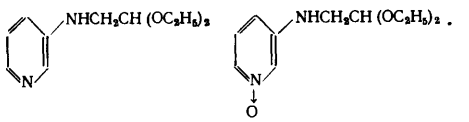


An interesting synthesis of porphobilinogen from 2-methoxy-5-nitro-4-methylpyridine (XLIII), proposed in 1965,[116] is based on Claisen condensation of the latter with oxalic ester followed by reductive cyclisation of the product (XLIV). Saponification of the methoxy-group in the resulting ethyl 5-methoxy-6-azaindole-2-carboxylate (XLV), introduction of a carboxyethyl group in position 3, and reduction of the pyridine ring with palladium gave the lactam of porphobilinogen-2-carboxylic acid (XLVI). Saponification of the lactam and decarboxylation enabled porphobilinogen (XIX) to be synthesised in an overall yield throughout the synthesis of 19%:



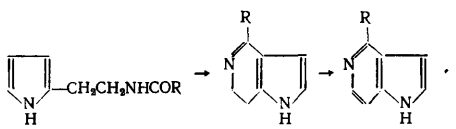
Methods of synthesising (XIX) suggested previously[112-115] gave yields not exceeding 2%.

Experiments on the cyclisation with polyphosphoric acid of 3-*N'*-diethoxyethylaminopyridines and their *N*-oxides, made by analogy with the synthesis of benzothiophens from aryl 2,2-dimethoxyethyl sulphides[117,118], did not give positive results in the case of azaindoles[25]:



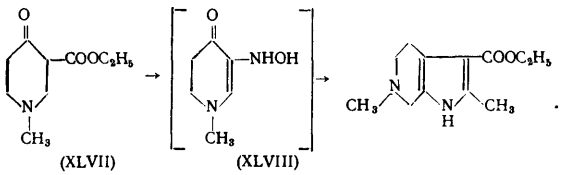
Attempts to cyclise 4-acetamido-3-bromopyridine to the corresponding 5-azaindole derivative[79] by the method of Hrutford and Bunnett[119] were also unsuccessful.

More interesting results have been obtained by synthesising 5-azaindole derivatives from acylated 2-2'-aminoethylpyrroles[120] by the Bischler–Napieralski reaction:

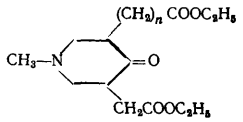


The acetyl and benzoyl derivatives were cyclised to the 4-methyl- and 4-phenyl-6,7-dihydro-5-azaindoles in yields of 18% and 24% respectively[27]. 2-*N'*-Formamido- and 2-*N'*-(3,4-dimethoxyphenylacetamido)-ethylpyrroles could not be converted into 5-azaindole derivatives[27].

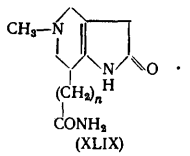
The synthesis of certain partly hydrogenated 6-azaindoles was accomplished by means of the reaction of ethyl 1-methyl-4-oxopiperidine-3-carboxylate (XLVII) with sodium nitrite, followed by reductive cyclisation of the 3-hydroxyimino-1-methyl-4-oxopiperidine (XLVIII) with acetoacetic ester[121]:



The cyclisation of other 1-methyl-4-oxopiperidines of general formula



by the action of ammonia has enabled several new 7-substituted 4,5,6,7-tetrahydro-5-methyl-5-azaoxindoles (XLIX) to be obtained, these existing in the oxo-form[122]:



III. CHEMICAL PROPERTIES OF AZAINDOLES

1. Chemical Peculiarities of Azaindoles due to Fusion of π-Electron-deficient and π-Electron-excessive Heterocycles in a Bicyclic System

A characteristic feature of azaindoles is that their fused bicyclic system is formed by two nitrogenous heteroaromatic rings with directly opposite displacement of the π-electrons inside each ring—the "π-electron-deficient" (in Albert's terminology[123]) pyridine ring and the "π-electron-excessive" pyrrole ring—and it is therefore interesting to examine the interaction of π-electron systems of this type and compare the chemical properties of azaindoles with those of the corresponding derivatives of pyridine, pyrrole, and indole.

Papers on the chemistry of the azaindoles have repeatedly noted their differences from indole compounds. In comparison with the latter, azaindoles have higher melting points[20], better aqueous solubility[20], and stability in acid and alkaline media[28,124], they do not give with a pine splint the colour reaction characteristic of indoles[30,73], and they exhibit more intense fluorescence[19].

Study of the basic strengths of unsaturated azaindoles revealed that three of them (4-, 5-, and 6-azaindoles) are stronger bases than is quinoline (pK_a 4.94), while 7-azaindole has a considerably smaller ionisation constant[20] (see Table 1).

The peculiarities of the 7-azaindole molecule in this case are due to the inductive effect on the 7-nitrogen atom of the closely placed 1-nitrogen[20]. An analogous effect is observed in benzimidazole (pK_a 5.53) and still more in indazole (1.22). Furthermore, the resonance contribution of *o*-quinonoid forms in 4- and 7-azaindoles is smaller than is that of *p*-quinonoid forms in 5- and 6-azaindoles, as a consequence of which the two former azaindoles have a lower pK_a value than have the latter isomers[20]. A

theoretical examination of the factors influencing the pK_a has enabled steric hindrance to be rejected in the case of 7-azaindole, since such hindrance would not be greater than in quinoline.

The ionisation constants of methylated 7-azaindoles[78], as was to be expected, are larger than that of unsubstituted 7-azaindole, diminishing in the sequence 4-, 6-, and 5-methyl-7-azaindoles (pK_a 5.23, 5.18, and 4.91 respectively).

Table 1.

Compound	M.p., °C	pK_a	λ_{max}, nm (lgε), in water
Indole	52	<1	273—278, 288(3.79+3.78; 3.69)
4-Azaindole	127	6.94	292 (3.92)
5-Azaindole	112	8.26	265.273 (3.59; 3.50)
6-Azaindole	135	7.95	260.291 (3.59; 3.68)
7-Azaindole	105	4.59	290 (3.91)

Examination of a large amount of information on the transmission of the effect of 1- and 6-substituents on the ability of 7-azaindoles and 7-azaindolines to undergo protonation at the nitrogen atom has shown[66,125] that a single aromatic system is present in 7-azaindoles, whereas in 7-azaindolines the effect of a substituent in the 1-position correlates well with the Taft induction constant for non-aromatic compounds. The application of correlation methods has enabled cross correlation equations to be obtained: for 1- and 6-substituted 7-azaindolines $-pK_a = -5.43 + 1.29\sigma^* + 8.0\sigma_i$, where σ^* and σ_i are the constants of substituents present in positions 1 and 6 respectively; and for 1- and 6-substituted 7-azaindoles $-pK_a = -3.80 + 8.57\sigma_{i\Sigma}$, where $\sigma_{i\Sigma}$ is the total constant of the substituents in positions 1 and 6.[66,125]

Table 2.

Compound	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	$J_{1,2}$	$J_{1,3}$
Indole	—0.12	2.73	3.55	2.45	3.00	2.92	2.60	2.5	2.
7-Azaindole	—	2.53	3.52	2.04	2.95	1.73	—	—	—
	$J_{1,4}$	$J_{2,3}$	$J_{3,7}$	$J_{4,5}$	$J_{4,6}$	$J_{4,7}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$
Indole	0.8	3.1	0.7	7.8	1.2	0.9	7.0	1.2	8.0
7-Azaindole	—	3.4	—	7.7	1.5	—	4.7	—	—

The good agreement between pK_a-values calculated by means of the correlation equations and those found experimentally shows that, in the case of 1- and 6-substituted 7-azaindoles and 7-azaindolines, the ionisation constants are influenced mainly by the induction effect of the substituents. A considerably smaller part is played by direct conjugation (except in 4-methyl-1-*p*-nitrophenyl-7-azaindole) and also by steric factors in these cases[66].

A special investigation[126] has been made of the nuclear magnetic resonance spectra of several heteroaromatic systems, including indole and 7-azaindole. However, this was confined to measurement of the proton chemical shifts and the spin–spin interaction constants, no attempt being made to characterise the distribution of electron density in azaindole systems (Table 2).

In order to examine theoretically the mutual influence of conjugated π-electron-deficient and π-electron-excessive rings in a fused system, the 7-azaindole[127] and indole[127,128] molecules have been calculated to the Hückel π-electron approximation. The results are presented in the form of tables (Table 3) and molecular diagrams (that of pyridine[129] is given for comparison):

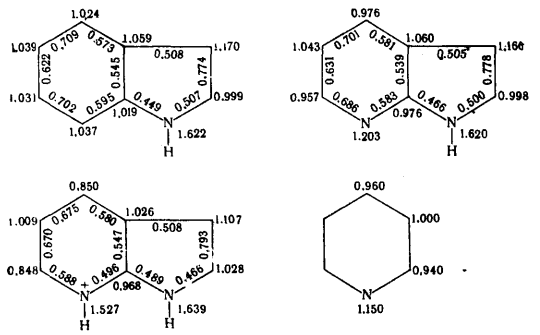


Table 3.

Compound	Vacant levels		Occupied levels		Total energy of π-electrons	Delocalisation energy	Resonance energy
Indole	—2.158	—1.179	0.534	1.280			
	—1.500	—0.853	0.796	1.669	13.399	11.399	3.399
				2.420			
7-Azaindole	—2.120	—1.174	0.571	1.366			
	—1.460	—0.770	0.829	1.702	13.847	11.447	3.408
				2.455			
7-Azaindolinium cation	—2.012	—1.044	0.742	1.603			
	—1.336	—0.481	1.022	2.174	16.944	11.844	—
				2.932			

From the distribution of effective charges it has been shown[127] that in the carbon portion of the 7-azaindole electrophilic substitutions should occur most readily at position 3, and nucleophilic substitutions at positions 4 and 6.

Comparison of the molecular diagrams of pyridine and 7-azaindole indicates[127] that, owing to the redistribution of charges in the 7-azaindole molecule, increased electron density is present at positions 4 and 6 compared with the corresponding positions 4 and 2 in the pyridine ring. This provides an explanation of the difficulty of nucleophilic substitutions in 7-azaindoles.

Chemical experiment has confirmed[66] that in 7-azaindole electrophilic substitution takes place most readily at position 3, while the sites of nucleophilic attack are the 4- and 6-carbon atoms. 7-Azaindole derivatives exhibit considerably less tendency to nucleophilic substitution in

comparison not only with pyridines but also with 7-azaindolines. For example[95], when 6-chloro-4-methyl-7-azaindole is treated with such a strong nucleophilic reagent as the methoxide ion, replacement of chlorine by methoxyl is only 39% complete even at 300°C. The analogous reaction with 6-chloro-4-methyl-7-azaindoline was more than 70% complete at 190°C, while the chlorine atom in 2-chloropyridine was replaced by the methoxy-group at only 70°C. 4-Methylpyridine reacts with *m*-nitrobenzaldehyde to give a 73% yield of *m*-nitrostilbazole, and the yield of styryl derivative when *m*-nitrobenzaldehyde is condensed under the same conditions with 1-butyl-4-methyl-7-azaindoline is 26%, while 1-butyl-4-methyl-7-azaindole does not react with aldehydes over a wide range of temperatures[93]. Nor have positive results been obtained from experiments[130] on the direct introduction of an amino-group into the 7-azaindole molecule in the presence of sodamide by the Chichibabin reaction, which is so characteristic of the pyridine series.

Electrophilic substitutions (the Mannich and Vilsmeier reactions, cyanomethylation, nitration, and bromination) are more difficult in position 3 of 7-azaindole derivatives than in the indole series. Groups present in positions 1 and 6 have a considerable effect here[66,131]. The ease of occurrence of these reactions increases, for example, on passing from 6-methoxy-7-azaindoles through the 6-unsubstituted compounds to 6-chloro-7-azaindoles[131], approaching in the last case analogous reactions in the indole series. The introduction of electron-acceptor groups into position 1 of the azaindole molecule hinders electrophilic substitutions in position 3, whereas electron-donor groups facilitate the process.

Substituents in positions 1 and 6 affect electrophilic substitution not only owing to change in the electron density at position 3 of the azaindole molecule but also because the ability of 7-azaindoles to be protonated at the pyridine nitrogen is changed[66,127]. The production, under the conditions of electrophilic substitutions, of forms in which the nitrogen atom is protonated leads to a general positive charge on the molecule and an associated redistribution of π-electron density, which, of course, hinders electrophilic attacks at position 3. This agrees well with calculation of the protonated form of 7-azaindole—the 7-azaindolinium cation[127].

2. Lactam–Lactim and Amino–Imino Tautomerism in 7-Azaindoles and 7-Azaindolines

Interesting results related to the interaction of the two nitrogen atoms in the 7-azaindole system have been obtained in a study of the lactam–lactim and amino–imino tautomerism of 6-hydroxy-7-azaindoles and also of 6-hydroxy-, 6-amino-, and 6-acylamino-7-azaindolines[66,132]. In contrast to other α(or γ)-hydroxy-*N*-heteroaromatic compounds, no sufficiently complete displacement of the tautomeric equilibrium towards the lactam takes place in 6-hydroxy-7-azaindoles and 6-hydroxy-7-azaindolines. In solutions comparable quantities of the two tautomers are observed, and ultraviolet and infrared spectroscopy permit the influence of the polarity of the solvent, and also the nature of the substituents attached to nitrogen in the five-membered ring, on the position of the lactam–lactim tautomeric equilibrium to be clearly traced[66].

With 6-hydroxy-4-methyl-7-azaindoline in dioxan solution 88% of the lactim form is observed, dilution with alcohol diminishes the content of the lactim, and in absolute alcohol the compound is almost completely converted into the lactam form. In the case of 1-butyl-6-hydroxy-4-methyl-7-azaindoline such conversion is already achieved in the range dioxan : alcohol (9 : 1)–alcohol : water (3 : 1). 6-Hydroxy-4-methyl-1-phenyl-7-azaindoline contains 88% of the lactim form even in a 1 : 1 mixture of alcohol and dioxan, while sufficiently complete conversion to the lactam form is accomplished only in water containing 2% of alcohol.

The presence of the two tautomeric forms of 6-hydroxy-7-azaindolines together is confirmed by the infrared spectra in dilute carbon-tetrachloride solutions, where both the carbonyl bands of the lactam form at 1630–1645 cm^{-1} and the absorption at 3580–3582 cm^{-1} characteristic of hydroxy-stretching vibrations of the lactim form are clearly developed.

The decrease in electron density on the 7-nitrogen on passing from pyridines through 7-azaindolines to 7-azaindoles is made evident in a further shift in the lactam–lactim tautomeric equilibrium towards the lactim forms in 6-hydroxy-7-azaindoles compared with 6-hydroxy-7-azaindolines[133]. Ultraviolet spectroscopic data indicate that in 6-hydroxy-4-methyl-1-phenyl-7-azaindole, for example, the tautomeric equilibrium is shifted so far towards the lactim form that considerable quantities of the lactim remain even in strongly polar solutions (in water containing 2% of alcohol). In this case neither in the crystals nor in dioxan solution can lactam groups be detected by infrared spectroscopy, and only in carbon tetrachloride, where the dielectric constant is higher than in dioxan, is a weak band at 1642 cm^{-1} due to the lactam carbonyl apparent together with the intense band at 3580 cm^{-1} characteristic of the hydroxy-group of the lactim form[133].

6-Hydroxy-derivatives of 7-azaindole and 7-azaindoline are distinguished from other α-hydroxy-*N*-heteroaromatic compounds not only in the position of the lactam–lactim tautomeric equilibrium but also in their chemical properties. For example, methylation with dimethyl sulphate in alkaline aqueous medium gives high yields not of *N*-methyl but only of *O*-methyl derivatives[66].

Investigation of the amino–imino tautomerism of 6-amino-4-methyl-1-phenyl-7-azaindoline and its $N_{(6)}$-acyl (acetyl, trichloroacetyl, and toluene-*p*-sulphonyl) derivatives by ultraviolet and infrared spectroscopy has shown that in this case the equilibrium is practically completely displaced towards the amino-forms, and even acylation with toluene-*p*-sulphonic acid does not lead to an appreciable shift in the tautomeric equilibrium towards the imino-form, in contrast to what happens with other *N*-heteroaromatic amines[66].

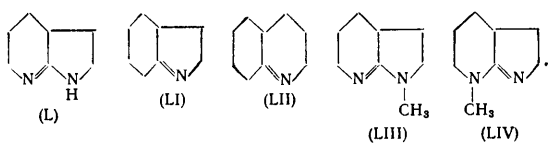
3. Substituted Azaindoles and Reduction of the Azaindole Ring

Synthetic investigations based on azaindole compounds developed by analogy with the chemistry of indole and pyridine. The various reactions were applied mainly to derivatives of 7-azaindole. Like the various pyridine bases, 7-azaindole forms salts (hydrochloride, picrate) and quaternary derivatives involving the nitrogen atom in the six-membered ring[28,124]; as in indole, the pyrrole nitrogen can be acylated and alkylated[95,124].

The hydrogenation of 7-azaindole by means of a nickel catalyst in decalin at 200°C and 118 atm yields 7-azaindoline[28]. 2-Amino-3-ethylpyridine was isolated as a side-product, and at higher temperatures became the chief product[134]. Analogous cleavage of the five-membered ring during hydrogenation at high temperatures is

observed also in the indole series[135]. 2-Alkyl-7-azaindoles are reduced under the same conditions with marked resinification, and satisfactory yields of 2-methyl- and 2-ethyl-7-azaindolines are obtained only with a copper–chromium catalyst[72]. Attempts to reduce ethyl 7-azaindole-1-carboxylate under mild conditions[134] did not yield positive results, unlike analogous experiments with other ethyl pyrrole-1-carboxylates[136].

The hydrogenation of 7-azaindole at room temperature and atmospheric pressure with a platinum catalyst yielded Δ^7-hexahydro-7-azaindole (L), whose structure was established by a comparative analysis of the characteristic C=N stretching frequencies in the infrared spectra of (L) and a series of analogous compounds[134]. It was shown[137–139] that in $\Delta^{8(1)}$-hexahydroindole (LI) the C=N stretching vibrations have a frequency of 1647 cm^{-1}, while the analogous C=N bond in $\Delta^{9(1)}$-octahydroquinoline (LII) is characterised by a frequency of 1658 cm^{-1}. The hexahydro-derivative of 7-azaindole investigated had an absorption band at 1652 cm^{-1}, while the hexahydro-derivatives (LIII) and (LIV) obtained by the reduction of 1- and 7-methyl-7-azaindole absorbed at 1657 and 1615 cm^{-1} respectively:



All these data indicate that, when 7-azaindole is hydrogenated in the presence of a platinum catalyst, the double bond in position 7(8) in the six-membered ring remains unreduced[134].

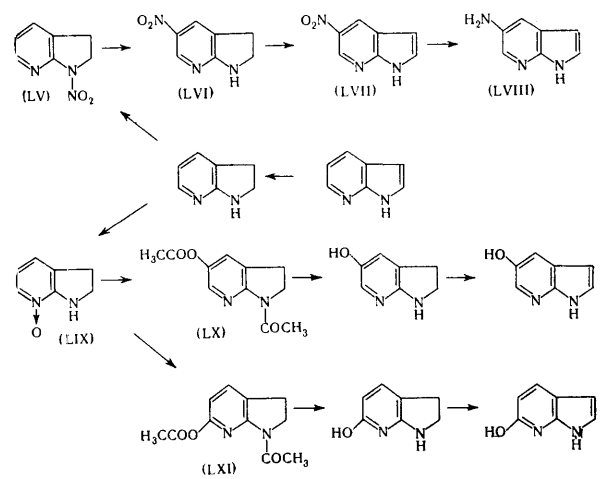
In contrast to 7-azaindole, the isomeric 5-azaindole could not be reduced in the presence of a platinum catalyst in acid medium[79].

When the 7-azaindole ring contains a 3-hydroxyimino-group, however, formation of 7-azaindoline derivatives is observed even in the presence of lithium tetrahydroaluminate[140].

4. Introduction of Substituents into the Pyridine Ring of Azaindoles

The conversion of 7-azaindoles into 7-azaindolines and the processes described above for dehydrogenating azaindoline derivatives have enabled a trial to be made in this series of compounds of an elegant method which has been widely used by Terent'ev, Preobrazhenskaya, and their coworkers in the chemistry of indole[141–144]. The method consists essentially in reducing indole or a derivative thereof to an indoline, which is an aromatic amine and hence capable of the usual reactions in the benzene ring. After the introduction of a substituent, the indoline is dehydrogenated, and the corresponding *Bz*-substituted indole is obtained.

This procedure has been used to introduce substituents at position 5 in 7-azaindole[130]. The 1-nitro-derivative (LV), obtained by nitrating 7-azaindoline, could be converted by thermal rearrangement into 5-nitro-7-azaindoline (LVI). The latter was dehydrogenated over palladium to 5-nitro-7-azaindole (LVII), from which 5-amino-7-azaindole (LVIII) was obtained by reduction. Another reaction used for the preparation of *Py*-substituted 7-azaindoles was rearrangement of the $N_{(7)}$-oxide of 7-azaindoline (LIX) in the presence of acetic anhydride. The rearrangement occurred unambiguously, and the corresponding 5- and 6-hydroxy-7-azaindolines were obtained as the *NO*-diacetyl derivatives (LX) and (LXI) in yields of 19% and 31%:[130]



In view of this, the directed synthesis of *Py*-substituted azaindoles[66] is more promising than the introduction of functional groups into unsubstituted azaindole structures.

5. Introduction of Substituents into the Pyrrole Ring of Azaindoles

Most work has been done on the preparation of 3-substituted 7-azaindoles. The 7-azaindoles are converted by the Mannich reaction into azagramines[66,77,131,145], the position of the 3-dimethylaminomethyl group in which has been confirmed by synthesis[77]. The nitration[66,77,131], bromination[66,131,146], and cyanomethylation[131] of 7-azaindoles have been described. The Vilsmeier reaction has proved a convenient general method for introducing a 3-formyl group into the 7-azaindole molecule[131,145,147]. The influence of the distribution of electron density and the nature of the substituents in 7-azaindoles on the above electrophilic substitution reactions has been considered above.

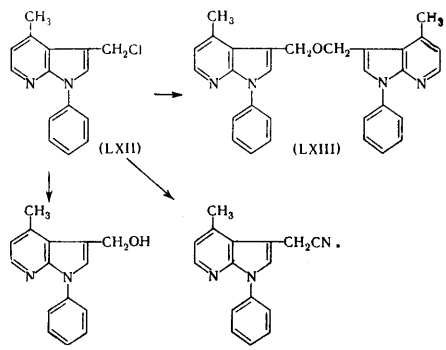
In the 5-azaindole series, in contrast to the 7-azaindoles, nitration, bromination, and other reactions did not give positive results. For example, various modifications of the Mannich reaction did not yield 5-azagramine[79]. Nor was it possible to synthesise[79] products of the reaction of 5-azaindole with piperidinomethylformamidomalonic ester by the method developed for the corresponding indole compounds[148]. Yet 2,5-dimethyl-4-azaindole undergoes electrophilic substitution at position 3 comparatively easily (even more readily than does 7-azaindole), which provided a method for preparing 2,5-dimethyl-4-azaindoles containing bromine, a nitro-group, formyl, and other substituents in position 3.[23] Information is lacking in the literature on the introduction of substituents into the ring of 6-azaindole.

The above peculiarities in the distribution of electron density in 7-azaindole govern not only the character of electrophilic substitution at position 3 but also the reactivity of substituents already present. For example, 3-bromo-7-azaindole, unlike analogous 3-bromoindoles, does not react with various nucleophilic reagents[146]. 7-Azagramine and its derivatives proved to be considerably weaker alkylating agents than the analogous gramines[145,146].

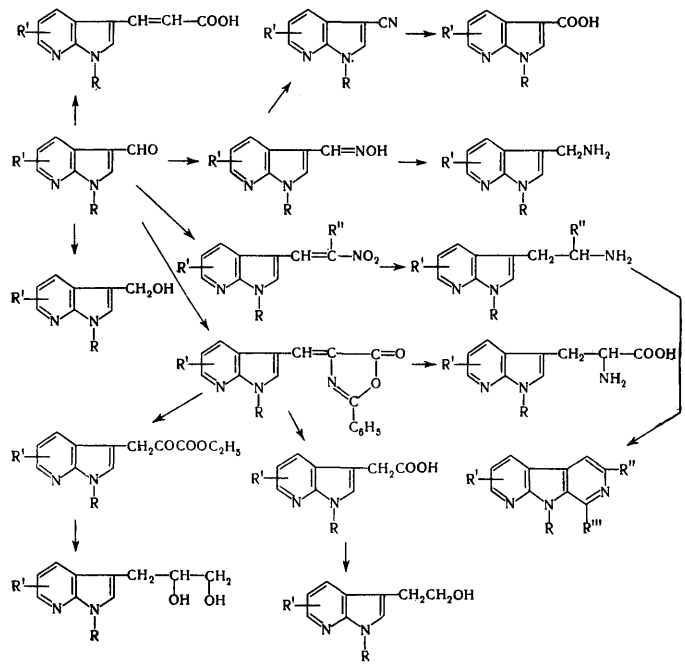
Although reaction of 7-azagramine with acetamidomalonic ester converts it into 7-azatryptophan[77], with malonic ester into 7-azaindol-3-ylpropionic acid[146], and with hydrocyanic acid into 7-azaindol-3-ylacetonitrile, syntheses based on 7-azagramines present certain difficulties. For example, even boiling unsubstituted 7-azagramine with hydrocyanic acid for many (64) hours does not raise the yield of 7-azaindol-3-ylacetonitrile above 49%.[146] Still lower yields were obtained in the analogous reaction with nitromalonic ester[146], and also in the reaction of substituted 7-azagramines with hydrocyanic acid[145].

In this connection considerable preparative interest attaches to 3-formyl-7-azaindoles[145,147] and the 3-chloromethyl-7-azaindoles which can be readily obtained from the former via the 3-hydroxymethyl derivatives[145]. The chlorine atom in the second series of compounds is allylic in character and is extremely labile. For example, it is replaced by hydroxyl even when the compound is dissolved in water, and can be titrated alkalimetrically[145].

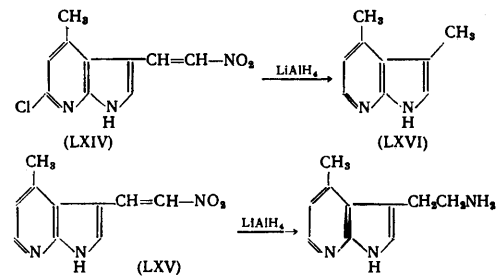
It is interesting that when, for example, 3-chloromethyl-4-methyl-1-phenyl-7-azaindole (LXII) is treated with potassium cyanide in 80% aqueous alcohol, bis-4-methyl-1-phenyl-7-azaindol-3-ylmethyl ether (LXIII) is formed in theoretical yield[145]. The cyano-group can be introduced only by the use of acetone cyanohydrin under anhydrous conditions[140]:



Comparison of various synthetic methods shows that the best results in the preparation of 3-aminomethyl derivatives are obtained by reducing the oximes of the corresponding 3-formyl-7-azaindoles with zinc in hydrochloric acid[140]. The most convenient method for the synthesis of 3-2'-aminoalkyl-7-azaindoles is to condense the 3-formyl derivatives with the nitroalkanes and then reduce with lithium tetrahydroaluminate in boiling tetrahydrofuran[66,101,107,140,149,150]. Other methods of synthesis, investigated by analogy with indole compounds (from 7-azagramines or 3-chloromethyl-7-azaindoles via the nitriles, cyanomethylation of azaindoles followed by reduction, from 3-formyl-7-azaindoles via the azlactones and amides of 7-azaindol-3-ylacetic acids), gave no advantages over these methods[66,151].



The course of the reaction of 6-chloro-4-methyl-3(2'-nitrovinyl)7-azaindole (LXIV) with lithium tetrahydroaluminate is unexpected: unlike the normal reduction of the dehalogenated compound (LXV), the reaction is accompanied by rupture of a carbon–carbon bond with formation of 4-methyl-7-azaskatole (LXVI)[150]:



The conversion of 3-formyl-7-azaindole into 3-cyano-7-azaindole by the action of nitropropane, ammonium phosphate, and acetic anhydride is interesting[152]. The mechanism of these reactions has not yet been studied.

The best method for obtaining 7-azaindol-3-ylacetic acids has proved to be from 3-formyl-7-azaindoles via the corresponding azalactones[66], for 7-azaindole-3-carboxylic acid from 3-formyl-7-azaindole via its oxime and 1-acetyl-3-cyano-7-azaindole[146], for 7-azaindol-3-ylacrylic acids from 3-formyl-7-azaindoles by the Knoevenagel and Wittig–Horner reactions[145], and for 7-azatryptophan derivatives by reducing the azlactones with hydriodic acid in the presence of phosphorus[66].

The reduction of 3-formyl-7-azaindoles and of 7-azaindol-3-yl-acetic and -pyruvic esters with complex metal hydrides provides a route for obtaining 3-hydroxymethyl[145], 3-2′-hydroxyethyl[66], and 3-(2,3-dihydroxypropyl)[145] derivatives of 7-azaindoles.

Acylation of 3-aminoalkyl-7-azaindoles followed by cyclodehydration yields derivatives of the new tricyclic system 1,7,9-triazafluorene[153]. Besides the fully aromatic triazafluorenes, the corresponding dihydro- and tetrahydro-derivatives have also been described[153].

IV. BIOLOGICAL ACTIVITY OF AZAINDOLE COMPOUNDS

Published information on the biological activity of azaindole compounds is still very sparse, and relates mainly to derivatives of 7-azaindole. It is interesting to note that the study of unsubstituted azaindoles led to the conclusion that there was no correlation between their pharmacological properties and such physicochemical characteristics as their ionisation constants, percentage ionisation at pH 7.4, or distribution in the ether–water system[18].

The examination of biological activity showed that in several properties competitive relations existed between indole and azaindole derivatives. For example, experiments with *Neurospora crassa* established that 7-azaindole inhibited the conversion of indole into tryptophan[154]. 7-Azatryptophan retards the assimilation of tryptophan by *Tetrahymena pyriformis*[155], and replaces tryptophan in reaction with the protein of the bacterium *Escherichia coli* and the bacteriophage T2,[156] by blocking the formation of carbamoyl-transferase and D-serine-deaminase[157]. It has been reported[18] that unsubstituted 7-azaindole, unlike indole, causes depression of the central nervous system, adynamia, and weakening of the smooth musculature in small laboratory animals. Another series of parameters established the similarity in the biological action of indole and azaindole compounds. For example, 7-azaindol-3-ylacetic acid proved to be a powerful plant growth hormone[158], similar to heteroauxin, and *laevo*-12-azadeserpidine[159] exhibited reserpinelike activity characteristic of natural deserpidine.

Nevertheless, as the investigations of S. S. Liberman (in M. D. Mashkovskii's laboratory in the All-Union Chemical–Pharmaceutical Scientific Research Institute) have shown[66], in several cases more complicated relationships than competing or similar activities were exhibited in the biological actions of indole and azaindole compounds. For example, in an experiment substituted 3-aminomethyl derivatives of 7-azaindole act similarly to tryptamine, and substituted aza-analogues of tryptamine exert a central depressive effect on the tone of the skeletal musculature, slow down motor activity, and produce a prolonged hypothermic effect. A pronounced hypotensive action, associated with the effect on the central nervous system, is possessed by aminoalkyl derivatives of 7-azaindole containing a longer aminoalkyl chain. Thus replacement of the 7-methine group in the indole ring by a nitrogen atom leads in several cases to the appearance of new pharmacological characteristics, sharply distinguishing azaindoles from analogous derivatives of indole.

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Chromatographic Resolution of Racemates on Dissymmetric† Sorbents

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The review discusses the use of natural sorbents (proteins, carbohydrates, and optically active quartz) and also artificial dissymmetric sorbents (based on silica gel and activated carbon) for the chromatography of racemates. Gas chromatography is very effective for the separation of diastereomers, but is less suitable for the direct separation of optical isomers. On the other hand, dissymmetric ion-exchange sorbents, which are considered in detail in the review, may find wider practical application. The list of references contains 197 items.

CONTENTS

I. Introduction 565
II. Chromatography of racemates on natural and inorganic dissymmetric sorbents 566
III. Resolution of racemates by gas chromatography 569
IV. Dissymmetric ion-exchange sorbents 570

I. INTRODUCTION

In connection with the vigorous development of research on the production of synthetic medicines, animal feeds, and food products, the problem of resolving various racemic compounds into optically active components has now become urgent. Chemical synthesis produces a racemic mixture of enantiomorphs, but usually only one form can be used for biological purposes.

A foreign dissymmetric agent is necessary for the resolution of a racemic compound‡. Use can be made of differences between the enantiomorphs in—(1) interaction with a dissymmetric environment (sorption on dissymmetric phases, diffusion through a medium containing dissymmetric centres, dissolution in optically active solvents, interaction with circularly polarised radiation or with polarised elementary particles, etc.); (2) rate of chemical interaction with optically active substances, and physical and chemical properties of pairs of diastereomers formed as a result of such interaction; and (3) interaction with a

† The term dissymmetric is to be applied to sorbents containing dissymmetric structural units possessing optical activity of definite sign (positive or negative). We recall that a structure is said to be dissymmetric if it contains no rotation-reflection axis of symmetry (an axis rotation about which, followed by reflection in a plane perpendicular to the axis, yields a structure identical with the original structure). Dissymmetry of structure is the necessary and sufficient condition for the appearance of optical activity in a substance. In determining the dissymmetric character of a molecule it is necessary to take into account all the conformations which the molecule can adopt under the given conditions. The selective absorption by a dissymmetric sorbent of one of the enantiomorphs of a racemate is to be termed stereoselective sorption.

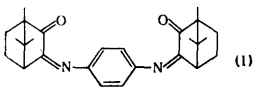
‡ The "spontaneous" resolution of racemates during crystallisation generally requires the introduction of a seed of an optically active substance.

living cell or its enzymes, which are capable of selectively assimilating or modifying one of the enantiomorphs of the racemic mixture.

Among all the methods enumerated[1], the resolution of racemates by chromatography on a dissymmetric sorbent is favourably distinguished by the theoretical possibility of quantitatively isolating both components of the racemate in optically pure form even if the dissymmetric sorbent used does not possess 100% optical purity[2]. This fact, coupled with the well known merits of the chromatographic method, suggests that the chromatographic resolution of racemates is quite promising for use on an industrial scale.

The possibility of resolving racemic compounds by stereoselective sorption of one of the enantiomorphs on a dissymmetric sorbent was first suggested by Willstätter in 1904.[3] By simulating dyeing processes for animal fibres, he tried unsuccessfully to detect the appearance of optical activity in a solution of a racemic alkaloid (tropacocaine, atropine, homatropine) in contact with the fibres. In such a case optical activity in the solution would have indicated preferential sorption of one of the enantiomorphs on the fibres. A difference in the sorbability of the optical isomers of a dye on wool was detected only in 1919 by Porter, first colorimetrically[4] and then by a polarimetric method[5].

In 1938 Henderson and Rule[6] first applied Tswett's chromatographic method to the resolution of racemic *NN'*-bis-2-oxoborn-3-ylidene-*p*-phenylenediamine


(I)

on a (+)–lactose column. In this case, the resolution of the racemate was due to the differing stabilities of the labile diastereomeric adducts formed with the enantiomorphs on the surface of the sorbent. The chromatographic method enabled these small differences in sorbability of the enantiomorphs to be clearly revealed, and showed the suitability of chromatography for the partial resolution of racemates.

Much research has been done during recent years on the problem of stereoselective sorption, these investigations having been partly surveyed in several review papers[7-14]. Therefore, while giving a full bibliography on these questions, we have discussed in greater detail only the most recent work in this field, and also the general features of the stereoselective sorption and the chromatography of racemates.

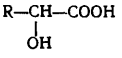
II. CHROMATOGRAPHY OF RACEMATES ON NATURAL AND INORGANIC DISSYMMETRIC SORBENTS

Natural proteins constituted the first dissymmetric sorbent used in studying the stereoselective sorption of enantiomorphs. In several cases some difference was confirmed in the sorbability of the enantiomorphs of racemic azo-dyes on the proteins of wool[4,5,15,16] or a difference in sorbability between the racemate and one of the enantiomorphs[17,18]. However, the effect observed under conditions of static sorption was extremely small, and the results obtained[4,5,15,16] could not be repeated on more careful checking[18-20]. Several workers report the absence of stereoselectivity in the sorption of azo-dyes on wool[20-22].

It was only in 1941 that Martin and Kuhn[23] demonstrated a separation of enantiomorphs sufficient for accurate observation in the case of mandelic acid, using an original device having a moving endless wool top. The optical activity observed in the acid solution in these experiments reached −0.35° and +1.0° at opposite ends of the apparatus.

A more detailed study of the sorption of racemic α-hydroxy-acids on wool was made during the 1950s by Bradley and his coworkers[8,24-28], who reached the conclusion[24,26] that an important part in this process is played by the free basic groups of L-lysine and L-arginine, which are present in considerable quantities in wool (the exchange capacity of wool with respect to acids reaches 0.45 mg-equiv. g^{-1}). This is supported by the sharp decrease in adsorption and in degree of resolution of mandelic acid when wool is used whose basic groups have previously been blocked by the radicals of some other acid[28]. It is indicated also by the inability of silk, which contains only minute quantities of diamino-carboxylic acids, to sorb selectively the enantiomorphs of racemic acids[17,18,22,24].

By studying the separation on wool of the isomers of a large number of racemic α-substituted glycollic acids



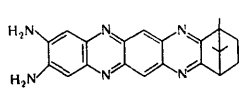
Bradley showed[24,26-28] that substituents R which are too large promote non-selective adsorption, and thus impair resolution of the racemic acid. Thus on passing in α-substituted glycollic acids from phenyl, substituted phenyl, and naphthyl radicals to *p*-hexadecyloxyphenyl and anthr-9-yl radicals the degree of separation of the isomeric acids is appreciably diminished. These facts make clear the reason for the failure of earlier attempts to detect the selective sorption of the large molecules of azo-dyes[18,20,21].

According to Bradley, important factors for the development of the selective sorption of α-hydroxy-acid enantiomorphs on wool are the presence of a free carboxyl and of an aromatic ring in the α-position[26,27].

It is interesting that, in all cases studied by Bradley[8,24-28] and by other workers[5,23,29], the dextrorotatory isomers of α-arylglycollic acids were more strongly retained by wool than were the laevorotatory isomers. It may be supposed that L-mandelic acid and its analogues containing substituted phenyl radicals and even other aromatic and heterocyclic substituents in place of the phenyl radical will possess a greater affinity for wool protein. Thus the accumulation and systematisation of experimental data on the chromatography of racemates may lead to the establishment of empirical rules for the assignment of dissymmetric compounds to known configurational series.

Slight selectivity of sorption for racemic azo-dyes[30], and to a greater extent for tryptophan[31], was observed with proteins of the serum albumin type. In contrast to mandelic acid[8], no separation of the enantiomorphs of α-bromopropionic acid was observed on casein[32].

There are indications of the non-selective sorption of the product (II) of the interaction of tetra-aminophenazine with camphorquinone isomers on protein tissues of living organisms[33].


(II)

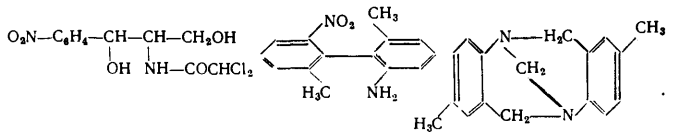
Grubhofer and Schleith[34] made successful use of a product obtained by coupling a protein with diazotised poly-*p*-aminostyrene for the partial resolution of racemic alanine.

Natural carbohydrates (lactose, cellulose, starch, sucrose) have been used in a considerable amount of work on the resolution of racemates. Carbohydrates contain no functional groups capable of electrolytic dissociation in

neutral media, and therefore the resolution of racemates on them is a consequence of intermolecular forces, an important part in these processes probably being played by hydrogen bonds.

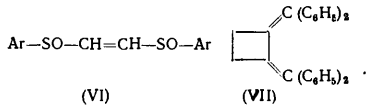
It has already been mentioned above that the chromatographic method was first used for the resolution of *NN'*-bis-2-oxoborn-3-ylidene-*p*-phenylenediamine (I) on a (+)-*lactose* column[6]. The resolving effect was very considerable. When the initial fractions of the eluate, enriched with the laevorotatory enantiomorph, were repeatedly passed through the column, the optically pure isomer was isolated after four cycles[19].

Lactose columns have been used for the partial separation of the isomers of chloromycetin (III)[35] and 1-amino-6,6'-dimethyl-1'-nitrobiphenyl (IV)[36], as well as Tröger's base (V)[37], which could not be resolved by other methods owing to its instability in acid media. The use of (+)-tartaric acid columns and those containing its potassium hydrogen salt gave a smaller effect[37].



(III) (IV) (V)

The molecules (IV) and (V) contain no asymmetric carbon atoms, their dissymmetry being due in the former to the non-coplanarity of the molecule and in the latter to the asymmetry of the rigid pyramidal structure of tervalent nitrogen attached to three different substituents. The similar pyramidal structure of sulphoxides is responsible for the existence of enantiomers in the *cis*- and *trans*-forms of 1,2-bisarylsulphoxyethylenes (VI), which also have been separated by means of (+)-lactose[38].



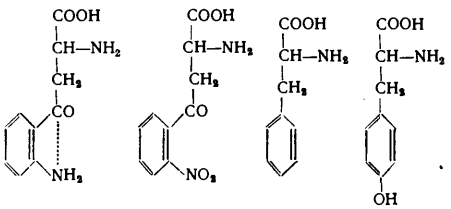
(VI) (VII)

Partial resolution on (+)-lactose has been observed with racemic lysine, its methyl ester and dihydrochloride, proline, tryptophan, glutamic acid[39], quaternary arsonium salts[40], and also the trisacetylacetonates of chromium and cobalt[41], yttrium and gadolinium[42], but not of iron, gallium, and indium[41]. Failure attended attempts to resolve the racemates of 1,2-bisdiphenylmethylenecyclobutane (VII) and its analogues[43], although the molecules of these compounds are non-coplanar.

In contrast to calcium (+)-tartrate, emulsin, maltose, glucose, and sucrose, (+)-lactose is able to resolve *m*-naphth-2'-ylazomandelic acid[21]. In some cases lactose can nevertheless be replaced by sucrose[39].

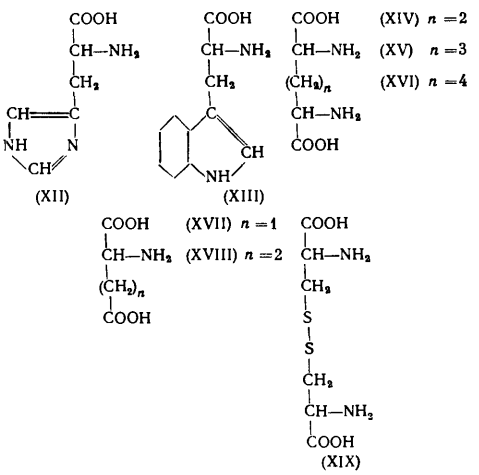
During the 1950s considerable progress was made in the resolution of racemates by chromatography on *cellulose* (paper). The first attempts to resolve racemic sugars were unsuccessful[44]. It was then found that preliminary treatment of the paper with (+)-camphorsulphonic acid[45] enabled the enantiomorphs of phenylglycine to be separated. In the presence of (+)-tartaric acid the isomers of 1-benzylamino-2-naphthol[46] and phenylalanine[47] are separated on paper. Some Japanese workers have subsequently found[48-51] that tyrosine, glutamic acid, and especially well tyrosine-3-sulphonic acid are resolved into two components even in the absence of foreign optically active substances. It was concluded that the reason was selective adsorption of the enantiomorphs on the paper, which was soon confirmed by the resolution of several other racemic amino-acids—kynurenine[52,53], α-hydroxytryptophan[54], tryptophan[52,55,56], histidine[56,57]—although Fujisawa[52] found that tyrosine (see, however, Refs. 49 and 50), leucine, phenylalanine, *N*-benzoyltyrosine, acetyltryptophan, and phenylalanine-*p*-sulphonic acid are not resolved on paper. In this connection it should be noted that the first worker to observe the resolution of a racemate by paper chromatography was obviously Dent[58], who as early as 1948 described the unexpected splitting of chromatographic spots of aspartic and glutamic acids.

An important contribution to elucidating the fundamental laws governing the resolution of racemates by paper chromatography was made by the work of Dalgliesh[59-61], who concluded that paper chromatography did not involve partition chromatography, as had previously been assumed[62], but represented a method of adsorption chromatography. Hydrogen bonds play an important part in the process of adsorption.



(VIII) (IX) (X) (XI)

Dalgliesh observed that racemic kynurenine (VIII) and 3-hydroxykynurenine[59] are successfully resolved on paper, but kynurenine which has been acetylated at either of the amino-groups, and also α-amino-β-benzoylpropionic acid and its *o*-nitro-derivative (IX), are not resolved[59,60]. Among phenylalanine (X) derivatives the 2,3-diol and the 2-methyl-3,4-diol are resolved, but phenylalanine itself, its 3,4-diol and 5-methyl-3,4-diol, and also tyrosine (XI) are not resolved (see, however, Refs. 49 and 50, which report partial resolution of tyrosine in the presence of amines). From these results Dalgliesh concludes that, for successful resolution of the racemate of an amino-acid, its molecule should contain a free carboxyl and a free amino-group. A planar aromatic ring having a small *ortho*-substituent can serve as third functional group to ensure three-point adsorption. The presence of a hydrogen bond between the amino-group and carbonyl in the kynurenine molecule (VIII) provides also a planar ring system in the β-position. However, whereas the L-series of isomers are more strongly sorbed among phenylalanine and tryptophan derivatives, the opposite situation is found for kynurenine derivatives.



(XII) (XIII) (XIV) $n=2$ (XV) $n=3$ (XVI) $n=4$ (XVII) $n=1$ (XVIII) $n=2$ (XIX)

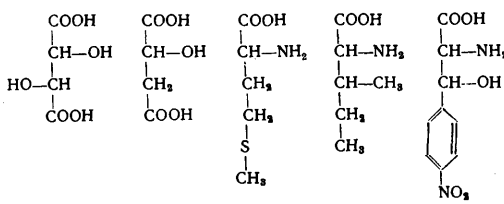
Dalgliesh's rules concerning three-point sorption are only approximate. They are consistent with the above resolution of histidine (XII) and tryptophan (XIII), but they cannot explain the fact that, among the dihydroxy-derivatives of phenylalanine, the 2,3-, 2,4-, 2,5-, and 3,5-diols are resolved, while the 3,4- and 2,6-isomers are not resolved[61,63]. Furthermore, it is obvious that the presence of an aromatic ring is not essential, since resolution on paper is observed for racemic $\alpha\delta$-diaminoadipic (XIV), $\alpha\epsilon$-diaminopimelic (XV), and $\alpha\zeta$-diaminoazelaic (XVI) acids[64], as well as partial resolution of aspartic (XVII)[58] and glutamic (XVIII) acids[48-51,58] and of cystine (XIX)[65].

A detailed study of the effect of the conditions of chromatography on the degree of resolution of racemic amino-acids has shown[65] that the best medium is 90% aqueous methanol without any addition of electrolytes. It has been found also that the separation of the enantiomorphs is appreciably improved by lowering the temperature to +2° and −15°C, a fact which was not explained[65]. Lowering the temperature to +4°C has an analogous effect also in the thin-layer chromatography of tryptophan and its derivatives on cellulose[66].

Partial resolution on paper has been reported for racemic catechin and epicatechin[67], complex cobalt(III) salts of glycine, alanine, and oxalic acid[68], pteridines[69], and also several alkaloids of the berberine[70,71]. Alessandro and Caldarera[72] described the resolution of the racemates of several physiologically active amines of the adrenaline group, but these results could not be repeated by other workers[73].

Chromatography on cellulose can be conducted also on a preparative scale in columns[67,69,71], but the degree of separation of the enantiomorphs then drops sharply[67,71].

The successful work of Krebs and his collaborators[74-82] has added yet another carbohydrate, *starch*, to the store of natural dissymmetric sorbents suitable for the resolution of racemates. This sorbent has proved capable of partly resolving into fractions having opposite optical rotation a large number of dissymmetric complex salts of cobalt and chromium containing two or three bidentate ligands such as glycine, dithiocarbamic acid, *p*-methylaminophenol, ethylenediamine, oxalic acid, etc.[74-77]. The resolution of these complexes was more effective on starch than on lactose, cellulose, sucrose, or wool[75,77].

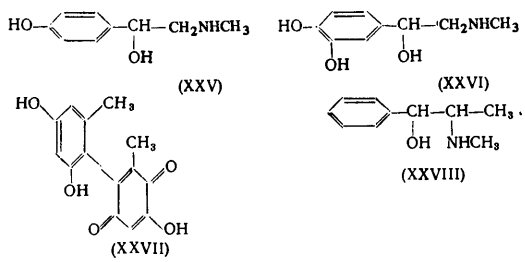


(XX) (XXI) (XXII) (XXIII) (XXIV)

Among organic substances the racemates of racemic acid (XX), malic acid (XXI) (optical purity 8%), and aspartic acid (XVII) (13%) are resolved on starch, but alanine, phenylalanine (X), methionine (XXII), isoleucine (XXIII), tryptophan (XIII), and β-hydroxy-β-*p*-nitrophenylalanine (XXIV) are not resolved[78-80]. These results agree well with Dalgliesh's rule on three-point adsorption established for paper chromatography. However, Krebs considers it valid only for flexible aliphatic molecules. The resolution of mandelic acid (optical purity 64.5%), phenylglycine (42%), phenylchloroacetic acid (50%), *O*-alkyl and *O*-acyl derivatives of mandelic acid, and also its esters shows that, with all these aromatic compounds having rigid molecules, the presence of two or even one functional group capable of forming hydrogen bonds with the hydroxyls of the starch is sufficient for successful resolution. Krebs regards molecular rigidity as the decisive condition for the successful resolution of isomers of such compounds[78-82]. This can be artificially increased by introducing additional bulky groups. Thus alanine, valine, and isoleucine are not resolved on starch, but their benzoyl derivatives are resolved. To resolve phenylalanine it proved sufficient to introduce into its molecule an acetyl or even a formyl group.

Krebs made the interesting observation that the best medium for chromatography on starch was water. The use of water–alcohol mixtures always diminishes the efficiency of the separation of isomers[78-80]. This fact has been confirmed by other investigators[83].

Ohara and his coworkers[84-86] have pointed out that, in all pairs of enantiomorphs of mandelic acid and its derivatives, the D-series of isomers—D(−)-mandelic acid $C_6H_5CH(OH)COOH$, (−)-methyl ester of D-mandelic acid, D(+)-acetylmandelic acid, D(+)-β-phenyl-lactic acid $C_6H_5CH_2CH(OH)COOH$, D(−)-tropic acid $C_6H_5CH(CH_2OH)COOH$—are the more weakly sorbed on starch. In the chromatography of atrolactic acid $C_6H_5C(OH)(CH_3)COOH$, on the other hand, the L(+)-isomer is eluted first. In view of this, these workers conclude that either the generally accepted assignment of (+)-atrolactic acid to the L-series is incorrect or else starch begins to develop a greater affinity for isomers of the D-series—not of the L-series—on passing from mandelic to atrolactic acid[85]. The latter hypothesis seems to us entirely plausible, because in mandelic acid and its derivatives the smallest substituent attached to the asymmetric carbon atom is a hydrogen atom, whereas in atrolactic acid the smallest substituent is a hydroxy-group. This marked change in molecular structure is fully able to explain the reversal in the order of sorption of these compounds.



(XXV) (XXVI) (XXVII) (XXVIII)

Partial resolution on starch has been reported for trichloroacetyl derivatives of α-amino-acids[83], phenylglycine[87], sympathol (XXV), adrenaline (XXVI), Henrich's quinone (XXVII)[88], and allylethylmethylphenylphosphonium bromide[89].

Reference has been made[90] to the possibility of resolving ephedrine (XXVIII) and 1-phenylethylamine by means of a copolymer of styrene and maleic acid which has been treated with thionyl chloride and then with glucose.

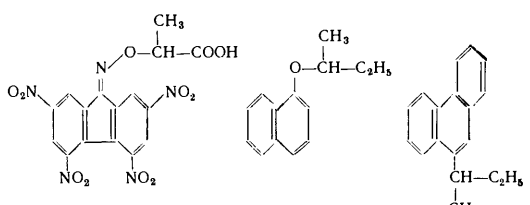
Finely ground crystals of *optically active quartz*, among inorganic dissymmetric sorbents, have been used for resolving racemates. Quartz is inert towards *m*-naphth-2′-ylazomandelic acid[19], *NN′*-bis-2-oxoborn-3-ylidene-*p*-phenylenediamine[6,19], and quaternary phosphonium salts[89], but several racemic complexes have been separated by means of quartz into fractions having opposite rotations. A partial separation has been effected of the oxahedral complex salts of cobalt(III) and chromium(III) with two or three bidentate ligands such as ethylenediamine, dimethylglyoxime, oxalate[91-96], and pentane-2,4-dione[97], and with

hexadentate ethylenediaminetetra-acetate[98], the tetrahedral complex of beryllium with benzoylacetone[99], and also potassium dinitro-*N*-methyl-*N*-ethylglycineplatinate[100] containing an asymmetric nitrogen atom.

Very little selectivity has been detected, during sorption on optically active quartz, of racemates of such neutral compounds as butan-2-ol[101], cyclic hydroperoxides[102], and quaternary arsonium salts[40,103]. The use[104] of this property of quartz for establishing molecular dissymmetry in compounds has been proposed. It has also been suggested[105] that the stereoselectivity of sorption can be determined by measuring the quantities of isomers sorbed from the vapour phase.

Sodium chlorate, like quartz, is able to form enantiomorphous optically active crystals. This property has been used by Ferroni and Cini[106] for the partial resolution of beryllium bisbenzoylacetonate. These workers report the possibility of resolving this complex directly on a commercial aggregate of sodium chlorate, which is a mechanical mixture of enantiomorphous crystals. They explain this phenomenon by the non-equivalent sorption of (+)- and (−)-forms of the complex on the corresponding forms of the crystals, which appears to us doubtful.

Methods have been described for preparing *silica gels* capable of the stereoselective sorption of optical enantiomorphs. Such silica gels contain "imprints" of the molecules of an optically active isomer of a substance which had been present in the reaction mixture during formation of the gel and then removed by extraction[107]. The presence of these "imprints" is due to the greater sorption capacity of the gel for the same isomer of this substance or of a structurally related substance than for their enantiomorphs. Thus silica gels have been prepared in the presence of optically active mandelic acid, (+)-camphorsulphonic acid[107,108], quinine and its enantiomorph quinidine[109], and also by hydrolysing optically active tetrakis-2-methylbutoxysilane, tetramenthyloxysilane, and tetrabornyloxysilane[110]. A silica gel containing "imprints" of quinine possessed greater affinity for quinine, cinchonidine, and other alkaloids of the same steric series than did silica gel having "imprints" of quinidine[109]. The selectivity of such sorbents falls with time.



(XXIX) (XXX) (XXXI)

Ordinary silica gel can also be given the properties of a stereoselective sorbent, by impregnating it with a solution of (+)-α-(2,4,5,7-tetranitrofluoren-9-ylideneaminooxy)propionic acid (XXIX). Racemates of esters and ethers, e.g. 1-s-butoxynaphthalene (XXX)[111], and even of hydrocarbons such as 9-s-butylphenanthrene (XXXI)[112] can be partly resolved on such a sorbent. In this case the adsorbent and adsorbate molecules form adducts of the picrate type, with the aromatic rings arranged parallel.

Aluminium oxide modified with optically active alanine, lactose, glucose, tartaric acid, sodium glutamate, menthan-3-ol, and fenchone was used by Karagounis[113,114], which enabled him to observe the weak resolution of mandelic acid, phenylglycine, camphor, etc.[114]. However, he was unable to resolve the free biphenylnaphth-1-ylphenylmethyl radical on these sorbents or on several other sorbents, undoubtedly owing to its planar structure[113].

Carbon modified with alkaloids has been used to separate the isomers of mandelic acid[115], and aluminium oxide modified with (+)-tartaric acid for separating chromium and cobalt acetylacetonates[97].

Thus, beginning in the 1920s, a large number of attempts have been made to resolve various racemic compounds on naturally occurring dissymmetric sorbents (proteins, carbohydrates, and optically active quartz) and also on silica gel, aluminium oxide, and activated carbon modified with optically active substances. The best results were obtained by using carbohydrates. In several cases it was possible to achieve quantitative resolution of a racemate by paper chromatography. However, on passing from purely analytical chromatography to the preparative separation of enantiomorphs on cellulose columns, the degree of separation fell sharply. On (+)-lactose and starch columns it has sometimes been possible to obtain fractions of isomers of optical purity ~ 50%, but an immense excess of the sorbent had to be used.

III. RESOLUTION OF RACEMATES BY GAS CHROMATOGRAPHY

Attempts have been made during recent years to apply the method of gas chromatography to the resolution of racemates.

The considerable advances made in the separation of various diastereomeric pairs by gas–liquid chromatography[116–135] have enabled highly sensitive methods to be developed for determining the degree of optical purity of optically active compounds, based on chromatography of the diastereomers formed by coupling these compounds with some other dissymmetric compound[130,131,135]. These methods have proved to be far more accurate than traditional measurements of specific rotation. The rapidity of an analysis and the great reliability of the results have permitted the use of gas–liquid chromatography for solving such complex problems as, for example, racemisation in peptide synthesis[136,137].

Here, however, we are more interested in direct separation of the components of a racemate by gas chromatography on an optically active phase. The first results in this field were obtained in 1959 by Karagounis and Lippold[138], who used (−)-ethyl tartrate or starch as adsorbent, and observed slight splitting of the peaks corresponding to racemic butan-2-ol, 2-bromobutane, ethyl α-bromobutyrate, and α-bromopropionic acid. However, in 1962 Japanese workers reported[84] that they were unable to repeat Karagounis' experiments on the separation of butan-2-ol by gas chromatography on columns containing starch, (−)-ethyl tartrate, or other optically active sorbents. Goldberg and Ross[139] also reported unsuccessful attempts to separate butan-2-ol, 2-chlorobutane, and 2-bromobutane on starch, (+)-1-methylheptyl sebacate, and methyl (+)-tartrate. They were unable to establish even partial separation of the enantiomorphs by measuring the optical activity of the fractions obtained by a preparative method of gas–liquid chromatography. Here these workers showed—what is extremely important—that racemisation of the optically active components does not take place under

analytical conditions. A paper[140] on the gas-chromatographic separation of the n-pentyl esters of *N*-acetyl-α-amino-acids on L-glutamic acid and sodium L-glutamate also does not report the splitting of peaks due to racemic compounds.

A detailed investigation of the possibility of separating by gas chromatography fifteen different racemates (carbohydrates, alcohols, alkyl halides, alkenes) on a series of optically active phases (sucrose octapropionate, heptamethylsucrose, menthyl stearate, and poly(propylene oxide)) was made by Goeckner[141]. In no single experiment was he able to observe splitting of the chromatographic peaks, in spite of his varying the temperature and the speed of the carrier gas between wide limits.

Nevertheless, Karagounis published a second paper[142] on the resolution of racemates by gas-adsorption chromatography on starch, sucrose, camphor-β-sulphonic acid, sorbitol, and (+)-trisethylenediaminecobalt(III) chloride, and also by gas–liquid partition chromatography on the optically active phases—(+)-dipentyl phthalate, ethyl (+)-tartrate, (+)-heptamethylsucrose, and (+)-heptamethyllactose—the racemates used being *trans*-1,2-dichlorohexafluorocyclobutane, 2-methoxybutane, and 3-hydroxybutan-2-one. In all cases the degree of separation of the enantiomorphs was extremely small. Nevertheless, in the preparative chromatography of *N*-methylpiperidine on sucrose two fractions of volume 0.3 and 0.5 ml were isolated, their optical rotations being respectively +0.100° and −0.120°.

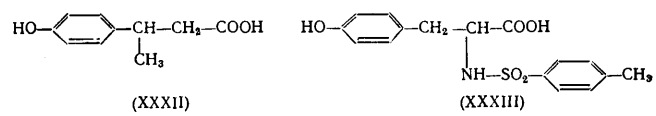
Complete separation of the isomers of racemic esters of the *N*-trifluoroacetyl derivatives of valine, alanine, and isoleucine was achieved only in 1966,[143] a capillary column of efficiency 75 000 theoretical plates being used. The optically active phase was the dodecyl ester of *N*-trifluoroacetyl-L-isoleucine. It was established that the degree of separation of the enantiomorphs increased with increase in the size of the alcoholic radical in the ester of the amino-acid. However, this was accompanied by an increase in the retention time, which reached 300–400 min, with almost complete blurring of the chromatographic zones. Besides this, the high temperature of the experiment (210°C) casts doubt on the lasting configurational stability either of the optically active phase or of the compounds undergoing separation.

Thus available information suggests that gas chromatography holds little promise for the resolution of racemates. On the other hand, the chromatography of diastereomers may prove of inestimable value as a rapid and accurate method of analysis.

The ineffectiveness of gas chromatography for the separation of optical isomers is explained, in our opinion, by the high temperature necessary for the analysis. The stereoselectivity of the sorption of enantiomorphs is determined by the difference in their energies of interaction with the dissymmetric phase. This interaction is characterised by weak intermolecular forces (induction, dispersion forces, hydrogen bonds, etc.), the effect of which falls rapidly with rise in temperature. Attempts to strengthen this interaction by introducing additional polar or bulky groups inevitably entail a rise in the boiling point of the racemate, and hence in the temperature of the chromatographic process. This difficulty cannot be removed within the limits of gas chromatography, but it does not arise in liquid chromatography. Such an explanation is consistent with the increase in degree of separation of enantiomorphous amino-acids noted above[65,66] with drop in the temperature of their chromatography on paper. The influence of temperature should appear especially clearly in paper chromatography, since here the process of sorption is not complicated by the temperature-dependent process of diffusion.

IV. DISSYMMETRIC ION-EXCHANGE SORBENTS§

In order to resolve racemic alcohols Macbeth and his coworkers[144] esterified them with dicarboxylic acids, and then prepared diastereomeric salts of the resulting acid esters with optically active alkaloids, an example being brucine 1-methylheptyl phthalate. Instead of the usual crystallisation, however, these workers successfully used a chromatographic method to separate the diastereomeric salts on a column filled with brucine. Although separation of the diastereomers takes place here mainly as a consequence of the difference in their solubilities in the solvent mixture employed, these workers correctly pointed out the theoretical possibility of ion-exchange reactions between the acid component of the salt and the brucine. This enabled them to propose the possibility of resolving racemates by means of synthetic dissymmetric ion-exchangers.



(XXXII) (XXXIII)

In 1952 Bunnett and Marks[145,146] synthesised dissymmetric ion-exchangers by the polycondensation of formaldehyde with optically active (+)-β-*p*-hydroxyphenylbutyric acid (XXXII) or *N*-toluene-*p*-sulphonyl-L-tyrosine (XXXIII). They showed in separate experiments that these compounds undergo no considerable racemisation under the conditions of polycondensation. However, all attempts to resolve racemic amines (*N*-methylpiperidine, 1-phenylethylamine, and γ-dimethylamino-αα-diphenylvaleronitrile) by means of these ion-exchangers in water and in ethanol were unsuccessful. Yet the accuracy of the measurements would have enabled even a slight (3%) enrichment of the eluate with one of the enantiomorphs to be detected. Discussing their results, Bunnett and Marks reject the possibility of the resolution of racemates by means of ion-exchangers containing in the macromolecule considerable aliphatic portions and only one ionogenic group for interaction with the ions of the substance to be separated.

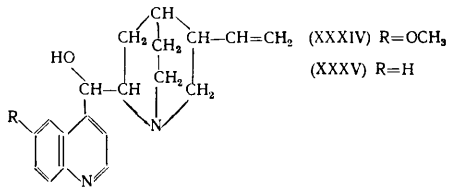
Failure attended an attempt to separate the isomers of mandelic acid on an anion-exchanger obtained by detaching the acetyl groups from the D-glucosamine units in the chitin macromolecule[147].

The successful resolution of racemic mandelic acid on a dissymmetric anion-exchange resin was first reported by Grubhofer and Schleith[34,148]. They converted the carboxyls in the cation-exchange resin Amberlite XE 64 (polyacrylic acid) into chlorocarbonyl groups, and esterified them with the secondary alcoholic groups of quinine (XXXIV). The exchange capacity of the resulting anion-exchange resin was low, 0.7 mg-equiv. g^{-1}. The isomers of mandelic acid did not separate on a column of the anion-exchange resin in aqueous and alcoholic media. On passing a 0.036 *N* solution of the acid in chloroform through the column, however, the percentage optical purity of the first

§ It has already been mentioned that naturally occurring proteins, e.g. wool, also contain ionogenic groups, which, perhaps, play an important part in the processes of sorption and chromatography.

few fractions, containing 4, 7, 16, 26, 34, and 43 micromoles of the acid, was found to be 100, 70, 44, 34, 31, and 30 respectively. The great defect of this exchanger is partial hydrolysis of the ester bonds even during its regeneration.

Krebs confirmed[80] Grubhofer and Schleith's results and used their anion-exchange resin to resolve complex salts of cobalt[77].



(XXXIV) R=OCH₃
(XXXV) R=H

Grubhofer's work was repeated by Klabunovskii[149], who also used quinine and the carboxylate cation-exchange resin KMG as starting materials. It is true that the maximum degree of enrichment with mandelic acid reached only 39% in his experiments, and was zero on the quite similar anion-exchange resin containing cinchonidine (XXXV). Attempts to employ an analogous anion-exchange resin with optically active ephedrine (XXVIII) were also unsuccessful.

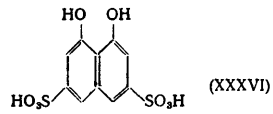
In 1959 Tsuboyama and Yanagita[150] described a dissymmetric anion-exchange resin of a different type: a styrene–divinylbenzene copolymer was subjected to chloromethylation and then to amination with (–)-1-phenylethylamine, which resulted in the introduction of secondary amino-groups into the copolymer. The capacity of the resulting anion-exchange resin was extremely small (0.43 mg-equiv. g^{-1}). On a column containing 10 g of this exchanger (4.3 millimoles) was sorbed 100 mg (0.66 millimole) of racemic mandelic acid, which was then eluted with 0.2 *N* aqueous ammonia. The resulting chromatogram consisted of two completely separate peaks, which were not equal in size. These workers state that the mandelic acid fraction corresponding to the second peak, and containing about 25% of the initial quantity of acid, consists of the practically pure dextrorotatory isomer. No explanation is given for the inequality of the chromatographic peaks.

We have tried to repeat Tsuboyama and Yanagita's results. However, no resolution of mandelic acid could be detected[2] on the high-capacity anion-exchange resin (3.36 mg-equiv. g^{-1}) which we have synthesised. The exchanger showed poor swelling in aqueous media, and retained practically no mandelic acid.

American workers have also been unable[151] to repeat the results of this work. Since Tsuboyama and Yanagita have published no further investigations on the chromatography of racemates, their results[150] must obviously be regarded as erroneous. Nevertheless, they aroused great interest in the ion-exchange chromatography of racemates.

A possible way of synthesising dissymmetric ion-exchangers is the polycondensation of optically active compounds containing basic or acidic groups. This method was used by Khromov-Borisov and Kozhevnikov[152], who effected the polycondensation of L-tyrosine with formaldehyde. They obtained insoluble polymers, since tyrosine reacted not only at the aromatic ring but also at the amino-groups, between which methylene bridges $NHCH_2NH$ or dimethyleneoxy-bridges $NHCH_2OCH_2NH$ were formed. The ability of the resulting exchangers to resolve racemates was not tested.

This was done by Losse et al.[153], who effected the polycondensation of formaldehyde with L-tyrosine in the presence of chromotropic acid



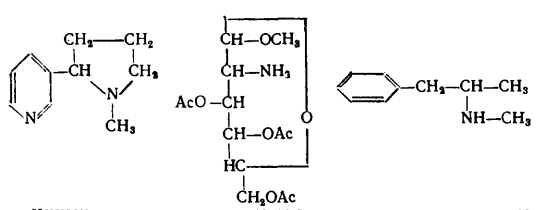
(XXXVI)

resorcinol, or *m*-toluidine. As a result, acidic or basic groups predominated in the polycondensate. The exchangers were tested for their ability to resolve racemic amino-acids—ornithine, lysine, valine, and glutamic and aspartic acids—for which purpose 1 g of the amino-acid in 10 ml of water (in the case of valine and the amino-dicarboxylic acids this could be assumed to be a suspension of the amino-acid in water) was sorbed on a column containing the exchanger, and eluted with 0.1 *N* hydrochloric acid or with water. In all cases the L-isomer of the amino-acid could be isolated from the eluate with an optical purity of 20–50%. The best results were given by the polymer obtained in the presence of resorcinol. The efficiency of separation of the isomers increased to a certain level with increase in the tyrosine content of the exchanger.

Another route has since been proposed for the synthesis of a dissymmetric cation-exchange resin containing residues of an optically active amino-acid[154]: cross-linked polyacrylic acid (Amberlite IRC-50) was converted into its acid chloride, and then treated with excess of L-aspartic or L-glutamic acid in boiling pyridine. The cation-exchange resins obtained in this way are capable of partly resolving racemates of diamino-carboxylic acids. By chromatographing lysine, for example, the D-isomer was isolated with an optical purity of 17%.

Analogous cation-exchange resins have been obtained by the radical polymerisation of optically active *N*-acryloyl-α-amino-acids or their esters[155]. In the latter case the carboxyl of the amino-acid is freed by heating the polymer with an acid (partial detachment of the amino-acid itself, bound to the polymer chain by an amide bond, is unavoidable).

A number of publications have described the synthesis of dissymmetric anion-exchange resins by the amination of chloromethylated styrene copolymers by means of various optically active amines, most often alkaloids. Thus Oda et al.[156] synthesised strongly basic anion-exchange resins, by using brucine and quinine. When a solution of mandelic acid was passed through a column containing the exchanger based on brucine, a fraction of the acid of optical purity 27% was isolated.



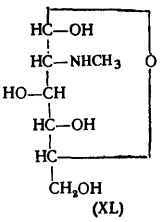
(XXXVII) (XXXVIII) (XXXIX)

Trochimczuk, Rabek, and Morawiec report an analogous synthesis of anion-exchange resins containing as dissymmetric components 1-phenylethylamine[157], cinchonidine (XXXV), nicotine (XXXVII), and ephedrine (XXVIII)[158,159]. Tsuboyama[160] used 3,4,6-triacetyl-1-methyl-D-glucosamine (XXXVIII) for the same purposes, and Selegny[161] has employed (–)-deoxyephedrine (XXXIX).

Lott and Rieman[151] used the laevorotatory isomer of *NN*-dimethyl-1-phenylethylamine for the amination of a

chloromethylated copolymer of styrene with divinylbenzene, and showed that the strongly basic anion-exchange resin formed possessed a greater affinity for (−)-mandelic acid than for its enantiomorph. Calculations based on a series of experiments with this exchanger indicate that a chromatographic column 2.3 km long would be required for complete separation of the isomers of mandelic acid.

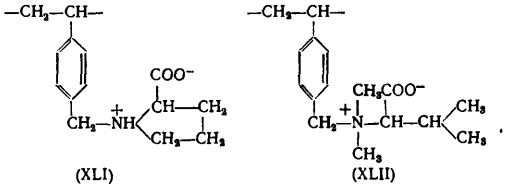
A patent[162] for the synthesis of ion-exchange resins based on cross-linked chloromethylated styrene copolymers proposes the use of a wide range of optically active amines and alkaloids—1-phenylethylamine, strychnine, ephedrine, *N*-methylglucosamine



(XL)

and also amino-carboxylic and amino-sulphonic acids or their esters.

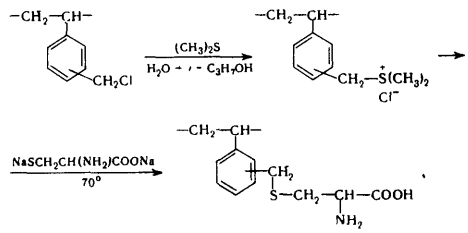
A series of dissymmetric ion-exchange sorbents based on α-amino-acids and copolymers of styrene with divinylbenzene has been synthesised by Davankov et al.[2,163,164]. Highly active bromo- and iodo-methylated copolymers were used for the synthesis, which enabled them to be aminated under mild conditions with amino-acids and their derivatives. Proline and *NN*-dimethylvaline readily undergo this reaction, forming amphoteric ion-exchange resins containing the units (XLI) and (XLII)



(XLI) (XLII)

It is advisable to use other α-amino-acids in the form of amides. Their interaction with halogenomethylated copolymers gives anion-exchange resins which can be converted into amphoteric exchangers by acid hydrolysis of the amide groups. Exchangers based on L-valineamide, L-leucineamide, and L-leucine have been prepared in this way. Chromatography of mandelic acid on these sorbents led to the isolation of small fractions of the optically pure dextrorotatory isomer of the acid. The isomers of proline undergo separation when its aqueous solution is run through a column of an exchanger based on L-proline.

Roberts and Haigh[165] synthesised an exchanger containing residues of optically active cysteine bound to a styrene copolymer by means of a sulphide bond:



The product possessed weak resolving power for racemic methionine.

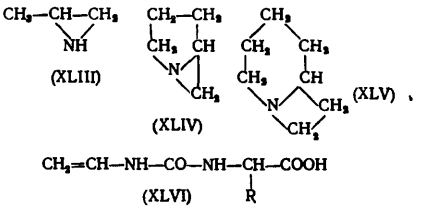
Papers by Manecke and his coworkers on the synthesis and examination of enzymatically active resins[166-168] have described nitrated copolymers of acrylic acid with its *m*-fluoroanilide, which, in virtue of the presence of a labile fluorine atom, could be combined with various enzymes or amines, in particular ephedrine. The anion-exchange resin obtained with L-ephedrine retained (+)-mandelic acid more firmly during chromatography, while the enantiomorph of the acid was eluted from the chromatographic column with optical densities up to 52.7%.[167]

Japanese workers[169] prepared a dissymmetric sorbent by the action of epichlorohydrin on chitosan, a product of the alkaline hydrolysis of chitin comprising oligomers of D-glucosamine. The sorbent obtained exhibited only very slight ability to resolve mandelic acid.

The use of carboxycellulose has been proposed[170] for the resolution of propylenediamine, and the product of the interaction of alkali cellulose with (−)-epoxypropyldeoxyephedrine for resolving racemic α-hydroxy-acids[171].

Attempts to resolve racemates by means of products of the reaction of poly-*p*-lithiumstyrene with nicotine, camphor, and camphorsulphonic acid have been unsuccessful[172].

Among the large number of optically active polymers which have been synthesised during recent years (for reviews see Refs. 173–175), a series of polyelectrolytes have been described which could in principle serve as foundation for dissymmetric ion-exchangers. Among them are the optically active polymers of 2-methylaziridine (XLIII),[176] 1-azabicyclo[3,1,0]hexane (XLIV),[177] and conidine (XLV).[178]



(XLIII) (XLIV) (XLV)

(XLVI)

Besides polypeptides (reviews[179,180]) we must include here polymers containing α-amino-acid fragments linked to the polymer chain by amide bonds at the amino-groups[181-183] or by ester bonds at the carboxy-groups[184], and also polymers of *N*-(vinylcarbamoyl)-L-amino-acids (XLVI)[185]. (Ionogenic groups in the polymers described in Refs. 182 and 184 can be freed by splitting off the protective groups.)

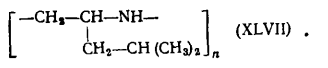
From our point of view the practical application of stereoselective sorption on a dissymmetric ion-exchanger is complicated by the fact that, in contrast to such sorbents as quartz, wool, starch, and cellulose, where we are dealing with dissymmetric active centres rigidly fixed on a solid surface, ion-exchangers when functioning have mobile solvated polymer chains. On the one hand, this tends to hinder formation of an adduct with the molecule undergoing sorption, which makes it necessary to impose specially rigorous requirements on the active centres of such a sorbent. On the other hand, it ensures that the sorbent shall operate throughout its bulk, which is shown in a considerably larger exchange capacity of the exchangers in comparison with other sorbents. This property makes dissymmetric ion-exchangers quite promising for the preparative resolution of racemates.

In our opinion the most suitable for these purposes are chromatographic systems having continuous circulation of the separable mixture through one or more columns. The initial and final fractions of a chromatographic zone are automatically withdrawn, and fresh portions of the mixture

are introduced into the middle of the zone, during each cycle. Such systems make even minute separation effects appreciable[186-188].

In connection with this problem it is interesting to mention the work of Toy et al.[189,190], who, foreseeing the need in the near future to convert amino-acids of the D-series into L-amino-acids, have synthesised resins which effect racemisation of optically active α-amino-acids. The desired isomer could be isolated from the racemic mixture, and the less valuable enantiomorph again subjected to racemisation. The process of racemisation is catalysed by resins containing units of the salicylaldehyde type, at pH 10.5 in the presence of copper ions.

Dissymmetric ion-exchangers can be used not only for the resolution of racemates but also as catalysts in asymmetric organic synthesis. This aspect of their application is shown by the work of Tsuboyama[160,191], who conducted a cyanohydrin synthesis in the presence of optically active polyisobutylethyleneimine

 (XLVII).

The benzaldehyde cyanohydrin (mandelonitrile) obtained in this way was laevorotatory, its optical purity reaching 11–19%. If a proportion of the amino-groups in the polymer were treated with isocyanate, the resulting polymer would catalyse the formation of the dextrorotatory cyanohydrin[191]. This phenomenon was explained by supposing that asymmetric catalysis was determined in this case not so much by the configuration of the asymmetric carbon as by the conformation of the whole polymer chain, which changed on passing from amine to amide nitrogen atoms in the chain.

Finally, dissymmetric sorbents may find application also in elucidating the mechanisms of chemical reactions and establishing the three-dimensional structure of compounds. Quite often only partial resolution of a racemate by a chromatographic method is sufficient for this purpose[91,100,192].

In conclusion we note the appearance of the first communications on the chromatographic *resolution of polymers*, containing asymmetric carbon atoms in the main chain[193,194] or in side-chains[195,196], into fractions of opposite rotation. Thus the separation of the crystalline polymer of 2-methyloxiran by means of polymeric (–)-menthyl glycidyl ether[193], and also by means of components containing sucrose, menthol, or borneol[194], has shown that the polymer consists mainly of enantiomorphous chains, and is not a stereo-block-copolymer. The analogous separation of poly-4-methylhex-1-ene adsorbed on optically active stereoregular poly-3-methylpent-1-ene[195] suggests that the polymerisation of racemic alkenes can be conducted not only as a stereospecific but also as a stereoselective process. Such separation of polymers differs, of course, from the chromatography of racemates of substances of low molecular weight in the fact that the polymeric product must in general be regarded not as a racemic mixture of enantiomeric chains but as a mixture of diastereomers[197]. It is noteworthy that, in contrast to poly-4-methylhex-1-ene, the monomeric analogue of its chain unit, 3-methylhexane, is not resolved on poly-3-methylpent-1-ene[196].

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Gas-chromatographic Methods for Studying the Kinetics of Liquid-phase Reactions

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A brief account is given of the main features of chemical reactions occurring in the stationary liquid phase in gas-chromatographic columns during the pulsed injection of the sample. Attention is paid mainly to the use of direct and indirect pulse methods of gas chromatography for determining the kinetic characteristics of reactions in the liquid phase.
The advantages and limitations of these methods are analysed. A promising future is shown for the wide application of pulse gas-chromatographic methods for the experimental study of the kinetics of liquid-phase reactions.

CONTENTS

I.	Introduction	576
II.	Main features of chemical reactions in chromatographic columns	577
III.	Chief experimental methods for studying the kinetics of liquid-phase reactions	580
IV.	Direct pulsed chromatographic methods for studying the kinetics of liquid-phase reactions	581
V.	Indirect pulsed chromatographic methods for studying the kinetics of chemical reactions	583

I. INTRODUCTION

Advances in the study of one of the main problems of modern chemistry—kinetics and the reactivity of chemical compounds—are governed in considerable measure by the development of new physicochemical methods and their wide practical incorporation in scientific investigations. Considerable progress in the study of the quantitative aspects of chemical reactions is due in particular to the wide use of gas-chromatographic methods in kinetic investigations [1,2].

Study of the composition of the reaction mixture is one of the most important tasks in experimental kinetic research. Although various physicochemical and chemical methods are employed to solve this problem, the most widely used techniques for analysing complicated multicomponent mixtures of volatile compounds are gas-chromatographic methods.

The simplest application of gas-chromatographic methods in research on kinetics consists in periodically withdrawing a sample of the reaction mixture from the reaction vessel, and then analysing it by gas chromatography. This is the mode of use adopted in most kinetic investigations.

An important characteristic of the chromatographic method is the possibility of studying the kinetics of a complicated chemical reaction at low degrees of conversion (under "pure" conditions), when the influence of the reaction products on the kinetics is negligible [3,4].

The first work on the application of gas chromatography to studying chemical kinetics by withdrawing and analysing samples of the reaction mixture was done during 1954–1956, [5-10] i.e. at the very start of the wide entry of gas chromatography into research practice. Gas chromatography is extensively used for studying the kinetics and the mechanism of chemical reactions because it possesses the following characteristics as an analytical method: (1) separation of the compounds under analysis is highly efficient (1000–5000 theoretical plates for packed columns, (20–100) × 10^3 theoretical plates for capillary columns); (2) the use of highly sensitive detectors enables small amounts of the reaction mixture (1–10 μl) to be employed for analysis, and the amount of component to be determined may be 0.01 mg for a catharometer and 10^{-4}–10^{-5} mg for a flame-ionisation detector; (3) the duration of an analysis is short, usually varying from a few minutes to several dozen minutes; and (4) standard chromatographic equipment is used for the separation.

In some studies of chemical conversion products, gas chromatography is used as a method of preparation, the compounds which are isolated on a preparative chromatograph being identified by other physicochemical methods [11]. Special mention must be made of the great opportunities for using gas chromatography in the analysis of radioactive and stable isotopes [12-15], which considerably extends the range of application of the method in kinetic investigations [12]. Methods have now been worked out for analysing the isotopes of hydrogen [14-18], the isotopes of oxygen [19], deuteriated methanes [20] and ethanes [21], and other labelled compounds [18].

By withdrawal of a sample from the reaction mixture and subsequent analysis, the gas-chromatography and the chemical process under investigation are isolated from one another, the former being used only as an efficient method of analysis. This method of applying gas chromatography to kinetics is by no means always the best, its wide use often being limited by several experimental difficulties: (1) kinetic investigations require the use as starting materials of pure compounds, and the amount of substance necessary for a kinetic experiment is often several grammes; (2) practical operation of the method is relatively simple only for slow reactions, rapid reactions requiring special methods to "freeze" the process; (3) gas chromatography can be used only to study the kinetics of reactions involving volatile components; and (4) the study of reactions occurring in viscous media is restricted by the difficulties involved in withdrawing the sample to be analysed and introducing it into the chromatograph.

Fundamentally new possibilities in studying the kinetics of reactions are opened up by pulse chromatographic methods, in which a plug of a volatile compound is injected into the carrier gas at the inlet to the reaction column, and the reaction occurring therein is assessed from the conversion or the retention time of the compound. In pulse methods the chemical reaction and the analysis are organically combined into a single method.

Two ways of applying pulse kinetic methods have been described, differing in the relation between the size of the plug of volatile reactant and the length of the active layer

in the reaction vessel. In the most widely used modification the plug is considerably smaller than the length of the layer, and in the other it considerably exceeds the length of the reaction vessel[22,23]. In the second variant there is practically no separation of the substances into individual zones along the layer. This method can be regarded as a microvariant of the usual flow technique for studying chemical reactions in a reaction vessel. We may mention also the possibility of using in kinetic investigations the method of reactant plugs, when reaction takes place in the reaction column between two plugs of volatile compounds, introduced successively into the column and moving along the reaction vessel at different speeds. In the literature the application of this method has been described only for analytical purposes[24].

In the kinetic study of reactions between a liquid and a volatile reactant (gas), investigation of the process under conditions of kinetic control is of especial interest. Various methods—e.g. vigorous shaking of the liquid phase in contact with the gaseous phase[25], bubbling the gas rapidly through the liquid[1], producing a thin layer of the liquid phase on the walls of the reaction vessel[26]—are used to accelerate diffusion processes in kinetic investigations of liquid-phase reactions in liquid–gas systems. When the reaction is conducted in a chromatographic reaction column, one of the reactants (the stationary liquid phase) is distributed as a thin layer (a few microns thick) on the surface of a macroporous inert carrier of surface 1–2 $m^2 g^{-1}$. On the assumption that blurring of the chromatographic zone is governed by the rate of mass exchange between gas and stationary liquid phase, the kinetic coefficient can be estimated by means of the relation[27] $\beta = 2\alpha/H$, in which α is the linear velocity of the carrier gas, and H the height equivalent to a theoretical plate. In practice we frequently have $\alpha \simeq 4$ cm s^{-1} and $H \simeq 0.2$ cm, so that $\beta \simeq 40$ s^{-1}. Thus it is probable that liquid-phase reactions having a rate constant $k \leqslant 1$ s^{-1} can be studied under kinetic conditions in a chromatographic reaction vessel.

Oxidation of an oil or other non-volatile product under the conditions of a chromatographic experiment, the liquid being applied as a thin layer to an appropriate porous carrier (glass, salt, metal), may be of interest for the rapid assessment of the working properties of technical products[28].

Pulse gas-chromatographic methods have been developed most widely and in greatest detail for the investigation of heterogeneous catalytic reactions. In several cases the results obtained can be used directly to examine the kinetics of liquid-phase reactions, for which gas-chromatographic methods are employed to a considerably smaller extent. Therefore the present review considers also work on the application of pulse gas-chromatographic methods to heterogeneous catalytic reactions where the results are of fundamental interest and can be used in studying liquid-phase reactions.

II. MAIN FEATURES OF CHEMICAL REACTIONS IN CHROMATOGRAPHIC COLUMNS

The pulse method was first suggested and employed by Kokes et al.[12] for the investigation of catalytic processes. Pulse chromatographic methods not only are more convenient and effective experimentally, but also provide fundamentally new opportunities for studying the kinetics and the mechanism of reactions.

A great contribution to the development of methods of reaction gas chromatography was made by Roginskii, Yanovskii, Gaziev, and their coworkers, who were the first to direct attention to the characteristics of chemical reactions occurring in chromatographic reaction vessels[29-35]. They showed that the kinetics of reactions occurring in chromatographic reaction columns are often so unusual that it is necessary in several cases to consider a special chromatographic régime of reactions, which differs fundamentally from the static and dynamic régimes.

For a reaction of the type $A \rightleftharpoons B + C$ with a pulsed supply of substance A to the reaction column, for example, the substances B and C are continuously generated and separated from A and from one another in zone A (the compounds A, B, and C move at different speeds along the reaction column), and form characteristic "peaks" outside the zone of the reactant A. Separation of reactant and products makes it possible to conduct the reversible reaction in one preferred direction, and to obtain yields of the desired product which considerably exceed the equilibrium yields under static conditions, etc. Under chromatographic conditions the chemical reaction takes place simultaneously (in conjunction) with chromatographic separation of reactants and products, which results in the process having the following characteristics: (1) owing to the separation it is mainly the initial reactant which is present in the reaction zone; (2) reversible reactions (e.g. of the type $A \rightleftharpoons B + C$) can be conducted predominantly in one direction, which enables yields to be obtained exceeding the equilibrium yields under static conditions; (3) the selectivity of the process is increased, the temperature of the reaction is lowered, side-reactions are eliminated, etc.; (4) the kinetic laws are simplified (e.g. the reaction zone contains practically no products which could act as poisons or promoters); and (5) new possibilities are opened up for studying the initial stages in the operation of a catalyst and for detecting intermediate products which are unstable under the reaction conditions[36].

If reaction of the initial volatile reactant is regarded as taking place in a system of coordinates moving at the speed of the reactant plug maximum in the reaction column, the reaction can be considered to occur in an open system in which the concentration of the initial volatile reactant continuously diminishes, and from which the reaction products are continuously removed (the rate of escape of the reaction products from the system is proportional to the difference between the velocities of the initial component and of the reaction products in the reaction column under the given experimental conditions). Reactions in open systems have several special characteristics[37]. In the present case an open reaction vessel of size proportional to the peak width of the initial reactant cannot be regarded as providing ideal mixing, since considerable concentration gradients of the reactants exist along its length. All this hinders an exact mathematical description of chemical reactions whose rate depends on the concentration of the products and the state of the catalyst.

Several specific physicochemical effects may occur during interaction between a solid catalyst and gases of variable composition, which are accompanied by a fundamental change in the results of the chemical process[38]. Continuous and pulsed supply of reactants produce different operating conditions for the catalyst, which may lead also to different results. In a study of the kinetics of the dehydrogenation of methanol[39], for example, similar results were obtained by the two methods. However, different kinetic parameters have been found[40] for the hydrogenation of acetone under conditions of pulsed and continuous reactant supply. Interesting results on the kinetics of the dehydrocyclisation of iso-octane and the hydrogenolysis of

mono- and di-alkylcyclopentanes have been obtained[41] by both methods, and a rational physical explanation is given of the observed differences for several types of reaction.

The above features of chemical reactions under pulse conditions are, of course, valid not only for catalytic but also for liquid-phase reactions. It must be emphasised only that, for the relatively wider range of liquid-phase chemical reactions, conducting the reactions in a chromatographic reaction column produces no change in the kinetics, as often occurs in the more complicated heterogeneous catalytic reactions.

In the case of slow irreversible reactions occurring in chromatographic columns, the zones of initial reactant and reaction products formed are now determined both by the chromatographic and by the kinetic characteristics of all the components in the reaction. For the reaction A → B, for example, the shapes of the zones due to the initial compound and to the product vary as a result of two processes—(1) ordinary chromatographic blurring during movement of the zone along the column, and (2) chemical reaction, during which the concentration of the initial compound in the chromatographic zone diminishes, while that of the reaction product increases.

Quantitative aspects of the formation of zones were discussed for the reaction A → B by Kallen and Heilbronner[42] on the basis of the theory of theoretical plates[43,44] within the framework of non-ideal linear chromatography. Equations were obtained[42] for the chromatographic zones of both the initial reactant compound and the product formed.

Let us examine the variation in concentration in the chromatographic zone of the initial reactant under conditions of equilibrium linear gas chromatography, caused by the action of longitudinal blurring factors. For a first-order reaction the initial equation can be written

$$\rho_G\frac{\partial c}{\partial t}+\alpha\rho_G\frac{\partial c}{\partial x}+\rho_L\frac{\partial a}{\partial t}+\rho_L k_L a=D^*\rho_G\frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where ρ_G and ρ_L are the fractions of gaseous and liquid phases in a cross-section of the column, D^* is the quasi-diffusion coefficient of longitudinal migration, and k_L is the first-order reaction rate constant in the liquid phase.

In view of the linear relation between the concentration in the liquid phase a and that in the gas phase c, we eliminate the variable a from Eqn. (1):

$$\frac{\partial c}{\partial t}+v\frac{\partial c}{\partial x}+k_{eff}\cdot c=D_{eff}\frac{\partial^2 c}{\partial x^2}, \qquad (2)$$

where

$$v=\frac{\alpha}{1+\Gamma\dfrac{\rho_L}{\rho_G}}. \qquad (3)$$

$$k_{eff}=\frac{k_L}{\dfrac{\rho_G}{\rho_L}\cdot\dfrac{1}{\Gamma}+1} \quad (4) \qquad D_{eff}=\frac{D^*}{1+\Gamma\dfrac{\rho_L}{\rho_G}}. \qquad (5)$$

If no reaction occurs, $k_L = 0$, and Eqn. (1) becomes

$$\frac{\partial\tilde{c}}{\partial t}+v\frac{\partial\tilde{c}}{\partial x}=D_{eff}\frac{\partial^2\tilde{c}}{\partial z^2}. \qquad (6)$$

The solution of this equation is[27]

$$\tilde{c}=\frac{c_0}{\sqrt{4\pi D_{eff}\,t}}\exp\left[-\frac{(x-vt)^2}{4D_{eff}\,t}\right]. \qquad (7)$$

We shall seek a solution of Eqn. (1) in the form

$$c=f(t)\cdot\tilde{c}. \qquad (8)$$

Substituting Eqn. (8) in (1), and taking into account Eqn. (6), we obtain for $f(t)$

$$-\frac{df}{dz}=k_{eff}\cdot f(t). \qquad (9)$$

Hence an approximate solution of Eqn. (1) is

$$c=\frac{c_0}{\sqrt{4\pi D_{eff}\cdot t}}\exp-\left[\frac{(x-vt)^2}{4D_{eff}\,t}+k_{eff}\,t\right]. \qquad (10)$$

Analysis of this equation shows that the retention time of the zone maximum and the temporal width of the zone vary somewhat as a consequence of the chemical reaction. However, for the usual conditions of a chromatographic experiment and slow chemical reactions, this variation is small.

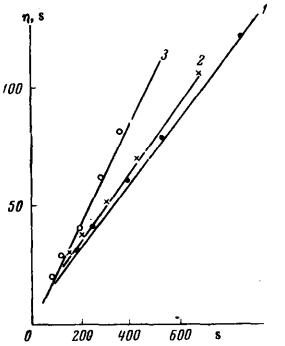

Figure 1. Dependence of peak width η on retention time for a mixture of hydrocarbons (in order of their elution from the column)—isopentane, pent-1-ene, isoprene, *cis*-piperylene, n-heptane— in a column (450 x 0.4 cm) containing as sorbent 10% of tritolyl phosphate and maleic anhydride (4:1) on a diatomite support at 70°C, with different velocities (ml min^{-1}) of the carrier gas: *1*) 31; *2*) 42; *3*) 65.

An experimental study has been made[45] of the blurring of the chromatographic zone of a reacting compound under the actual (non-equilibrium) conditions of gas–liquid chromatography. In order to ascertain whether this blurring is specific, the dependence of the peak width η on the residence time t in the column was determined simultaneously for the peaks due to a non-reactant and to a reactant[46]. It was supposed that, if the point (η_r, t_r) for the reactant did not lie on the $\eta = \eta(t)$ "calibration" curve obtained for non-reactant compounds, the specific blurring of the peak due to the chemical reaction could be estimated quantitatively; otherwise, it could be concluded that the reaction had no specific effect on the blurring of the chromatographic peak. Fig. 1 shows the dependence of peak width η on retention time for various hydrocarbons and various velocities of the carrier gas (31–65 ml min^{-1}). No specific blurring of the zone representing a reactant compound (isoprene) was detected (for constants of 5–16 $M^{-1}\,h^{-1}$ and degrees of conversion of 30–70%).

Roginskii and Rozental'[47] obtained a solution for the more general case in which a first-order homogeneous reaction in the gas phase and a heterogeneous catalytic reaction, of the first order with respect to the surface concentration of adsorbed reactant, occur simultaneously in the chromatographic reaction vessel. In this case the

reactant concentration distribution along the column should satisfy the set of equations

$$\frac{\partial p}{\partial t}+\frac{\partial a}{\partial t}+u\frac{\partial p}{\partial x}+k_1 p+k_2 a=0$$
$$\frac{\partial a}{\partial t}=k_3 p-(k_2+k_4)a, \qquad (11)$$

where p is the number of reactant molecules per unit volume of the gas phase (which is proportional to the partial pressure of the reactant gas), x is the distance along the column from the point of entry of the gas into the column, a is the number of adsorbed reactant molecules per unit volume of the gas phase, u is the linear velocity of the carrier gas in the column, and k_1, k_2, k_3, and k_4 are the rate constants of the homogeneous reaction, the heterogeneous catalytic reaction, adsorption, and desorption respectively.

If the chemical reaction takes place in a film of the stationary liquid phase, the above set of equations and the consequent solution can be extended to reactions in gas–liquid chromatography, provided that $k_3=\beta$ and $k_4=\beta/\Gamma$, where β is the kinetic coefficient and $\Gamma=a/p$.

The partial pressure of the reactant gas before entering the column is a known function of time $\psi(t)$, with $\psi(t)=0$ at $t=0$ and $t\geqslant t_e$. At the inlet to the column $\psi(t)=p(x,t)$ at $x=0$.

If the time required to introduce the reactant gas into the reaction column t_e is close to zero, the solution obtained for the chromatographic zone of the reactant at $t-x/u\gg t_e$ was

$$p(x,t)=\frac{2xm_0k_3k_4\exp\left[(k_3-k_1-k_2+k_4)\frac{x}{u}-(k_3-k_4)tJ_1(z)\right.}{uz}, \qquad (12)$$

where

$$z=2\sqrt{k_3\cdot k_4\frac{x}{u}\left(t-\frac{x}{u}\right)}$$

m_0 is the initial quantity of reactant gas, and $J_1(z)$ is the first-order Bessel function of the first kind in an imaginary variable. For large values of the variable we have

$$J_1(z)=e^z/\sqrt{2\pi z}\ .$$

For values of x which satisfy the condition $x/u>3k_3k_4(k_2+k_4)$ the retention time of the reactant compound is given by the formula[47,48]

$$t_{max}=\frac{x}{u}+\frac{k_3\cdot k_4x}{2u(k_3+k_4)^2}\left[1+\sqrt{1-\frac{3u(k_3+k_4)}{k_3\cdot k_4x}}\right]. \qquad (13)$$

This equation shows that a homogeneous reaction does not affect the retention time.

A more general solution for the mean residence time of reactant molecules in a chromatographic reaction vessel and for the dispersion of the chromatographic zone has been obtained by Denisova and Rozental'[49]. These workers, in discussing first-order chemical reactions under pulse conditions, take into account the diffusion of gas molecules, and show that diffusion combined with the chemical reaction diminishes the mean residence time of unchanged molecules in the reaction vessel and also the width of the peak.

The characteristic kinetic laws for reactions of different orders ($n\neq 1$) under conditions of pulse chromatography were first examined by Gaziev et al.[50] On the assumption that reaction occurs under conditions of ideal linear chromatography, they examined the diminution in concentration of the initial reactant for reactions of zero, first, and second orders and for pulses having different forms. In the case of a first-order reaction the degree of conversion was unaffected by the shape of the pulse, but for zero- and second-order reactions it does depend on the form of the pulse at the inlet to the reaction vessel.

The fact that the degree of conversion is independent of the form of the pulse for a first-order reaction under conditions of gas-chromatographic separation has received experimental confirmation[51], in which the degree of conversion of butadiene by reaction with maleic anhydride was determined from the areas of the peaks due to the reactant compound and from the heights of multistage peaks. In Fig. 2 the heights of the chromatographic zones (steps) preceding and following the reaction vessel (h_1/h_2) are plotted along the horizontal axis, and the ratio of the areas of the peaks (S_1/S_2) along the vertical axis. It is seen that the same results are obtained in the two cases: i.e. the form of the pulse does not affect the degree of conversion. In the study of first-order reactions, therefore, the degree of conversion can be measured by the ratio of peak areas, which is more convenient in practice.

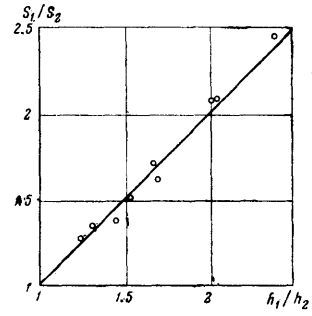

Figure 2. Dependence of S_1/S_2 on h_1/h_2 for butadiene at temperatures of 55.5°, 60°, and 74°C.

The field of application of the pulse gas-chromatographic method to liquid-phase reactions is considerably extended by using as a second reactant (the stationary liquid phase or a solution of a non-volatile component in it) a substance having a measurable vapour pressure at the temperature of the experiment. When the experiment is conducted under steady-state conditions, the loss of volatile substance from the column must be balanced by establishing the same concentration of this substance in the flow of carrier gas before the sample inlet. In this case reaction will take place in two phases—liquid and gaseous—and it is interesting to examine methods for determining separately the reaction rate constants in them. Assuming that the rates of chemical reaction can be described in both phases by a first-order equation, and that the reaction is kinetically controlled, let us examine the variation in the quantity of volatile substance (plug) resulting from passage through the reaction vessel, which is actually measured in an experiment. We remember that the superposition principle is satisfied (Eqn. 1):

$$W=\frac{dm}{dt}=\frac{dm_G}{dt}+\frac{dm_L}{dt}=F\rho_G\int_0^L w\,dx+F\rho_L\int_0^L w\,dx \qquad (14)$$

in which

$$w=k_G c_B^l c \qquad (15)$$

$$w=k_L a_B^n a \qquad (16)$$

$$a=\Gamma c \qquad (17)$$

where k_G and k_L are the reaction rate constants in gas and liquid phases respectively, c and a are the corresponding concentrations of the volatile component, c_B and a_B are those of the second, less volatile component (practically constant under the experimental conditions), F is the cross-sectional area of the column, and ρ_G and ρ_L are the fractions of gas and liquid phases in the cross-section of the column. Let us rearrange Eqn. (14) to give

$$W = F[k_G\rho_G c_B^l + k_L a_B^n \Gamma\rho_L]\int_0^L cdx. \quad (18)$$

The total quantity of volatile component in the column satisfies the relation

$$\int_0^L cdx = \frac{m}{F(\rho_G + \Gamma\rho_L)} \quad (19)$$

and consequently

$$\frac{dm}{dt} = \frac{k_G\rho_G c_B^l + k_L a_B^n \Gamma\rho_L}{\rho_G + \Gamma\rho_L} \cdot m = k_{eff} \cdot m \quad (20)$$

where

$$k_{eff} = \frac{k_G\rho_G c_B^l + k_L\Gamma\rho_L a_B^n}{\rho_G + \Gamma\rho_L}. \quad (21)$$

Equation (20) is analogous to the differential rate equation for a first-order reaction.

Since, when detectors are used in the range of the linear scale, the quantity of substance is directly proportional to their area on the chromatogram, it follows that

$$\ln\frac{m_0}{m} = \ln\frac{S_0}{S} = k_{eff}\,t \quad (22)$$

where S_0 and S are the areas of the peak due to the volatile reactant on the chromatogram in the absence of the reaction vessel and after passing through it.

Let us make a more detailed examination of the equation for k_{eff}, having written it in the somewhat different form

$$k_{eff} = \frac{k_G\rho_G c_B^l/\rho_L + k_L\Gamma a_B^n}{\rho_G/\rho_L}. \quad (23)$$

All the terms in Eqn. (23) other than the rate constants can be determined. The separate determination of k_G and k_L requires that measurements should be made with different reaction vessels, characterised, for example, by different proportions of liquid and gaseous phases.

For stationary phases (reactants) which are either completely or nearly non-volatile, we note that $a_B \gg c_B$, and the first term in the numerator of Eqn. (21) can be neglected, so that

$$k_{eff} = \frac{k_L a_B^n}{\rho_G/\rho_L \cdot 1/\Gamma + 1}. \quad (24)$$

According to Ref. 27, we have

$$\rho_G/\rho_L \cdot \frac{1}{\Gamma} = \frac{t_0}{t_{corr}} \quad (25)$$

in which t_0 is the dead time of the reaction column and t_{corr} is the corrected retention time; therefore

$$\ln\frac{S_0}{S} = k_L a_B^n t_{corr}. \quad (26)$$

In the other extreme case, in which reaction takes place solely in the gas phase, and a flow of carrier gas containing a constant concentration of one reactant passes through a tube containing no sorbent, we find that

$$\ln\frac{S_0}{S} = k_G c_B^l t. \quad (27)$$

The theory of reversible chemical reactions of the type $A \rightleftharpoons B + C$ occurring under conditions of ideal linear chromatography in a column has been discussed by Magee [52]. A theoretical investigation of the effect of reaction velocity on the retention time and the form of the eluted peak has been made by Klinkenberg [53] for reactions of the type $A \rightleftharpoons B$. A closely related problem has also been analysed [54].

III. CHIEF EXPERIMENTAL METHODS FOR STUDYING THE KINETICS OF LIQUID-PHASE REACTIONS

The variation in concentration (quantity) of the components of a reaction can be studied by direct and indirect methods. In direct pulse chromatographic methods the rate of a chemical reaction is assessed from a direct determination of the quantity of a reacting component, and in indirect methods from the dependence of the retention parameters of unreactive components on the composition (quantity) of the reaction mixture used as the stationary liquid phase.

Table 1. Various forms of pulse gas-chromatographic methods for studying the kinetics of chemical reactions.

Reactants volatile	One reactant volatile, others non-volatile	All reactants non-volatile
1. Two volatile components enter reaction column together. Method has been used to study the kinetics of catalytic reactions [55]. 2. One component injected as plugs into reaction column, while the second enters the reaction vessel continuously in the stream of carrier gas. Method suggested in Ref. 50. 3. Plug of one component injected into reaction column, and after a definite time interval a plug of the second component. Reaction occurs during the time in which the second overtakes the first component in the reaction column.	4. Volatile component injected into column in plugs, while non-volatile compounds used as stationary liquid phase, either directly [56] or as solution in non-volatile solvent [51]. 5. Volatile component introduced continuously into column, while non-volatile components used as stationary liquid phase. Into the reaction column are periodically injected plugs of a standard mixture of non-reactants, the variation in whose retention times indicates the composition of stationary liquid phase (indirect method) [58].	6. Starting materials used as stationary phase in reaction column. Plugs of mixture of standard non-reactants periodically injected into column, the variation in their retention times indicating the variation in composition of the stationary liquid phase resulting from reaction (proposed [58] indirect method).

Pulse chromatographic methods of kinetic investigation are applicable to various chemical reactions, but the choice of the optimum method depends on the state of aggregation and the volatility of the reaction components, as well as on the type of reaction. Some of the main modifications of the method for reactions of the type $A + B + \ldots \rightarrow C + D + \ldots$ are listed in Table 1. It can be seen that pulse gas-chromatographic methods can be successfully applied to a wide range of reactions, the components of which are in various states of aggregation. It must be stressed that Table 1 indicates only the chief variants: for example, it does not reflect experimental methods of using volatile products to study the kinetics of non-volatile compounds, which are especially promising for the kinetic examination of the degradation of polymers.

The arrangement of the kinetic chromatographic apparatus is varied depending on the method of kinetic study and the type of reaction. Table 2 gives some of the principal block diagrams. Switching devices (valves, multiway taps, etc.) are not shown in these diagrams.

Table 2 illustrates four main types of scheme, differing in the relative arrangement of chromatographic column and reaction vessel. When it is necessary to work with labelled atoms, these schemes must be supplemented by detectors to record the labelled compounds (e.g. Geiger counters).

Table 2. Some fundamental block schemes for studying the kinetics of chemical reactions.

Chromatographic schemes	Characteristics of scheme
1	Simple chromatographic scheme. Column is also reaction vessel.
2.1, 2.2, 2.3, 2.4	Reaction vessel preceded by chromatographic column, which is used to obtain a plug of the pure reactant. Trap used if necessary to constrict plug of initial volatile reactant. Column and reaction vessel may be located in different thermostats. The most universal scheme of this type is 2.4.
3.1, 3.2	Reaction vessel followed by column to separate initial reactants and reaction products.
4	Combined scheme, enabling pure substances to be obtained before entering the reaction vessel, and substances to be analysed after leaving it.

○ 1 ⋀⋀⋀ 2 □ 3 △ 4 ⊠ 5 ● 6

Conventional symbols: *1*) device for injecting sample; *2*) chromatographic column; *3*) detector having two measuring cells; *4*) measuring unit with pen-recorder; *5*) reaction vessel; *6*) trap.

In the design of chromatographic apparatus for kinetic studies account must be taken of the following possibilities in conducting an experiment—(1) "preparative" (in analytical quantities, of the order of milligrammes and fractions of a milligramme) chromatographic production of the pure initial reactant, (2) mixing of one initial reactant with others, (3) injection of the reaction mixture as a sharp plug (instantaneous introduction) or as a rectangular pulse of finite duration (step), or else continuous introduction of one or more reactants into the reaction vessel, (4) chromatographic separation of the reaction products and determination of their concentration both before and after the reaction, and (5) stabilisation of the reaction conditions (temperature, rate of flow of carrier gas, etc.).

An important advantage of direct pulse gas-chromatographic methods for studying the kinetics of liquid-phase reactions is the possibility of using impure substances as starting materials, these being separated from impurities by chromatography immediately before the reaction. This increases both the reliability and the universality of the method. Rephrasing Ostwald's well known statement, we can say that pulse chromatographic methods enable accurate results to be obtained when using contaminated starting materials.

It may be noted that kinetic chromatographic equipment can be assembled very quickly by using standard parts (thermostats, detectors, columns, measuring devices, etc.) of gas chromatographs.

IV. DIRECT PULSED CHROMATOGRAPHIC METHODS FOR STUDYING THE KINETICS OF LIQUID-PHASE REACTIONS

A direct method for the kinetic study of liquid-phase reactions was first used by Gil-Av and Herzberg-Minzly in investigating the reaction of conjugated dienes with chloromaleic anhydride[56]. A plug of the diene was introduced into the flow of carrier gas before the latter entered the reaction column (dimensions 200 × 0.4 cm) containing the chloromaleic anhydride. It was shown that the reaction was not controlled by diffusion, and corresponded to a first-order kinetic equation. From measurements of the rate constants at two temperatures (25° and 40°C) the activation energy was found to be 17.2 and 15 kcal mole^{-1} for *trans*-penta-1,3-diene and isoprene respectively, these values agreeing with published data.

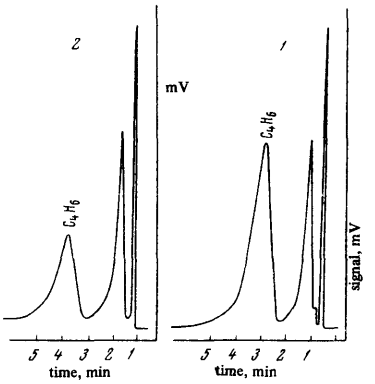

Figure 3. Chromatograms of butadiene:
1) preceding the reaction vessel; *2*) following the reaction vessel.

This method has been developed[51] to determine the order of reaction with respect to a second, non-volatile component and the rate constant of a bimolecular reaction. Scheme 2.2 in Table 2 was used for the experimental work, in which the kinetics of the reaction between dienes and maleic anhydride was studied. Fig. 3 shows as example the chromatograms of butadiene before and after reaction with maleic anhydride. The peaks eluted from the column before the butadiene are due to air and butenes present as impurities in the butadiene. The second component in the reaction—maleic anhydride—was deposited on brick as a solution in tritolyl phosphate saturated at 45°C. This choice of solvent had the aims of—(1) extending the temperature range of the reaction (since the melting point of maleic anhydride is 55°C, so that it cannot be used as a reactant in the liquid phase below this temperature), (2) increasing the retention time and hence the period of contact of the reactants, and (3) investigating the kinetics of the reaction with respect to the non-volatile component, i.e. maleic anhydride.

The kinetic measurements were made at a constant concentration of maleic anhydride, which exceeded by factors of 10^2–10^4 that of the volatile component, butadiene. Not more than 0.02% of the maleic anhydride reacted during one experiment. Reaction in the gas phase had no appreciable effect on the observed results. Kruglikova and the Reviewer have shown that, for this reaction at 69°C, $k_G\rho_G c_B/k_L\Gamma\rho_L a_B \simeq 10^{-4}$, so that the gas-phase reaction can be disregarded.

Degree of conversion was determined from the change in the areas of the chromatographic peaks preceding and following the reaction vessel. The slight blurring which occurs when the plug of the substances passes through the reaction vessel should not affect the results, since with a first-order reaction the relative conversion does not depend on the form of the plug. The bimolecular rate constant was calculated by means of Eqn. (26), the concentration a_B being varied [57]. This equation was used to determine the kinetic characteristics of the Diels–Alder reaction of butadiene, isoprene, and penta-1,3-diene with maleic anhydride. Under the given conditions these reactions are practically irreversible [59].

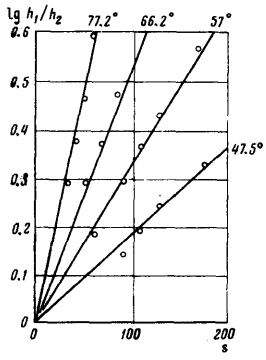

Figure 4. Dependence of logarithm of degree of conversion of butadiene on time of reaction at various temperatures.

Fig. 4 shows the dependence of the logarithm of the degree of conversion of butadiene on its contact time with maleic anhydride at various temperatures. The contact time of the reactants was calculated as the difference between the retention times of the diene preceding and following the reaction vessel, with the dead time of the latter taken into account. The straight lines obtained confirm that, with a constant concentration of maleic anhydride, the reaction obeys a first-order equation with respect to the diene.

The order of the reaction with respect to maleic anhydride can also be determined by this method. For this purpose different concentrations of maleic anhydride in tritolyl phosphate were used in a series of experiments, and the logarithm of the maleic anhydride concentration $\lg c_{MA}$ was plotted against $\lg y$, where $y = \lg(S_0/St_{corr})$. Fig. 5 illustrates this relationship for the reactions of maleic anhydride with butadiene and with isoprene. The slopes of these straight lines show that the order of the reaction with respect to maleic anhydride differs slightly from unity (slightly greater with butadiene, and slightly less than unity with isoprene), which is probably due to the influence of the solvent used.

The activation energies of the reactions were determined graphically from the linear dependence of the logarithm of the rate constant on the reciprocal of the temperature. Activation energies were evaluated by this method for the reactions of butadiene, isoprene, and piperylene with maleic anhydride. Table 3 gives values determined by the pulse chromatographic method for the rate constants and the activation energies of these reactions, and includes for comparison available published values of the activation energies calculated from the quantity of diene remaining unchanged, as in the case of a second-order reaction [60]. The rate constants differ somewhat from the published values, but are of the same order of magnitude, while the activation energies for butadiene and isoprene are practically identical with the published values. The results in Table 3 are mean values for whole series of experiments. Individual values of the constants do not differ from their mean value by more than 10%. Thus rate constants and activation energies for bimolecular reactions can be determined quite accurately by the pulse chromatographic method.

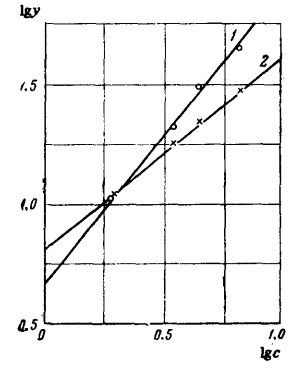

Figure 5. Dependence of $\lg y$ on $\lg c$ for: *1*) butadiene; *2*) isoprene.

Table 3. Rate constants and activation energies for reactions of dienes with maleic anhydride.

Diene	Reaction rate constants k, $M^{-1}\,h^{-1}$, at temperatures (°C)									Activation energy, kcal mole^{-1}	
	47.5	49	51.3	57	59.6	60.5	66	68.3	69.6	77	found	Ref. 60
Butadiene	1.55			2.8			4.7			7.9	12±0.8	11.7±0.8
Isoprene		5.75			11.0			16.9			12.1±1	12.2
Piperylene			8.5			12.4			16.7		8.1	—

The rate constants of these reactions can be determined on chromatographic apparatus having a single detector if the reactant concentration is measured relative to an unreactive reference substance introduced into the mixture:

$$k_L = \frac{2.3 \lg \dfrac{S_{01}/S_{1ref}}{S_{02}/S_{2ref}}}{c_B^n t_{L\,corr}} \qquad (28)$$

where S_{01}/S_{1ref} is the ratio of the areas of the chromatographic peaks for the diene and the reference material on the column (in the absence of the reaction vessel), and S_{02}/S_{2ref} is the corresponding ratio when a reaction column

is used. Rate constants obtained by this method for the reaction of isoprene with maleic anhydride are practically identical with results obtained by other methods.

Pulse methods can be applied also to studying the kinetics of isotopic exchange. They have been used[61] to produce deuterium-labelled compounds (ketones containing a labile hydrogen atom) on a semi-preparative scale. The compound labelled with deuterium was formed during passage of a plug of the volatile compound through a gas–liquid chromatographic column filled with Gaschrom Z (100–120 mesh) which had been coated with 10% Carbowax 6000 and 10% potassium deuteroxide KOD. The column (3 m long) was used for the semi-preparative production of deuterated compounds after the initial injection of 0.3 ml of D_2O and stabilisation for a few hours. A table is given[61] indicating the conditions of deuterium exchange and the degree of exchange.

A pulse chromatographic method has been used also to study the kinetics of the esterification with acetic anhydride of various alcohols having high boiling points[62]. The volatile reactant (acetic anhydride) entered the reaction vessel in the form of a plug, while the non-volatile reactant (the alcohol) was present in the reaction column as the stationary liquid phase. In contrast to the application of the pulse method to diene syntheses, in the esterification of an alcohol with acetic anhydride one of the reaction products (acetic acid) is eluted from the reaction column after the initial component (acetic anhydride).

The reaction vessel used was a chromatographic column of size 100 × 0.4 cm. The non-volatile alcohol was deposited on fluorinated plastic A (1 : 10 by weight). The purity of the initial alcohols was checked chromatographically. Esterification of the alcohols was studied over the temperature range 80–130°C, since the rate of esterification is small at lower temperatures, and at higher temperatures the alcohols begin to volatilise appreciably from the column.

Table 4. Kinetic characteristics of the esterification of alcohols with acetic anhydride.

Reactant	Rate constants		Activation energy, kcal mole^{-1}
	first order k_I, min^{-1}	second order k_{II}, M^{-1} h^{-1}	
Dodecan-1-ol	1.12*	14.8*	17
Hexadecan-1-ol	0.73**	12.9**	19
Heptadecan-9-ol	0.099**	1.9**	24
Cyclododecanol	0.22**	3.0**	15
7-Methyltridecan-7-ol	0.041*	0.65*	23

* At 104°C. ** At 100.7°C.

A mixture of acetic anhydride and the reference material (benzene) was introduced as plugs into the chromatographic reaction column, where the test alcohol was used as the stationary liquid phase. Different degrees of absorption of the acetic anhydride were obtained by varying the speed of the carrier gas. The time of contact of the reactants was determined as the difference between the retention time of the acetic anhydride and the dead time of the reaction column.

The first-order rate constants with respect to acetic anhydride were determined by the method of least squares from the linear dependence of $\lg(S_0/S_{ref})$ on the period of contact.

Table 4 shows that primary alcohols have the highest esterification rate constants, while tertiary alcohols are esterified much more slowly under the same conditions, secondary alcohols occupying an intermediate position with respect to their reactivity. The activation energies of these reactions were determined from the temperature dependence of the rate constants, and are included in Table 4.

The above examples indicate the promising future for the wide application of direct pulse methods in the kinetic study of liquid-phase reactions.

V. INDIRECT PULSED CHROMATOGRAPHIC METHODS FOR STUDYING THE KINETICS OF CHEMICAL REACTIONS

The above methods for studying the kinetics of liquid-phase reactions cannot be used with reactions involving only compounds which are non-volatile or which are unstable at high temperatures, i.e. compounds for which direct gas-chromatographic analysis is impossible under the reaction conditions. However, analysis is often a complicated problem for such systems.

A new form of gas chromatography—inverse gas chromatography—has been used to study the kinetics of chemical reactions in such systems[63,64]. In contrast to the usual form of development chromatography, the substance to be analysed is the stationary liquid phase, and a mixture of known standard compounds of various types is separated on it. In inverse chromatography the substances and mixtures under analysis (stationary liquid phases) are characterised mainly by the retention parameters of the components of the standard mixture. The stationary phase (test compound) is characterised by a spectrum of retention parameters of the standard compounds. The method can be applied both for group identification and for determining the quantitative composition of simple mixtures[63,64].

In a proposed method[58] for studying chemical kinetics, the reaction occurs in the chromatographic column, and the reaction mixture is used as stationary liquid phase for a standard mixture of non-reactants. Variation in the composition of the reaction mixture with time is checked by periodic measurement of the elution characteristics (e.g. the relative retention times) of the non-reactants. Thus determination of the composition of the reaction mixture is based on a relation of the type

$$c_i = f(\tau_j) \qquad (29)$$

where c_i is the concentration of one of the components in the reaction mixture, and τ_j is the relative retention time of a standard non-reactive compound. The inverse relation $\tau_j = \psi(c_i)$ has been studied by several investigators in connection with the problem of using binary mixed liquid phases for separating complicated mixtures of volatile compounds[65–68].

Results given in most of the papers indicate a linear relation between the relative retention parameter and the concentration of one of the components in the binary stationary phase. In general, however, this relation must be regarded as non-linear, which was correctly pointed out in Ref. 68.

If some physical property (in the present case the retention time τ) is proportional to the concentration of a substance in the reaction mixture, we have

$$\tau = \tau_\infty + (\tau_0 - \tau_\infty)\frac{c}{c_0} \qquad (30)$$

where τ, τ_0, and τ_∞ are the retention times of some substance on the reaction mixture (the stationary liquid phase)

respectively at time t, at the start of the reaction, and when the reaction is complete. In this case the kinetic equation for a unidirectional first-order reaction can be written[37]

$$k = \frac{2.3}{t} \lg \frac{\tau_0 - \tau_\infty}{\tau_t - \tau_\infty} \quad . \qquad (31)$$

The indirect pulse method of studying kinetics has several advantages: it does not require the removal of samples, and only small amounts of the test substances are needed, of the order of a few milligrammes in the case of capillary columns; it can be used to investigate the kinetics of reactions in systems which cannot be analysed chromatographically because of thermal instability or non-volatility; and it enables kinetic investigations to be made in various systems—solid–liquid, liquid–liquid, liquid–gas—and also for various catalytic reactions.

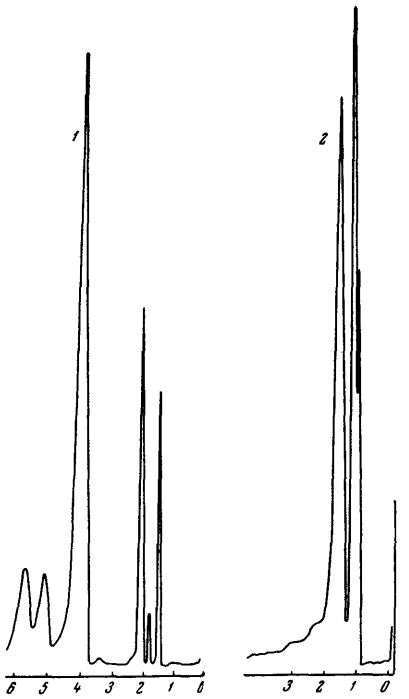

Figure 6. Chromatograms of standard mixture of butenes on: *1*) original benzaldehyde; *2*) completely oxidised benzaldehyde.

An example of the use of this method is the kinetic investigation of the oxidation of benzaldehyde to benzoic acid. The usual chromatographic apparatus was used for the kinetic study[69]. Air was passed at a rate of 30 ml min^{-1}, to act both as oxidant and as carrier gas, through a chromatographic column (200 × 0.4 cm) filled with diatomaceous brick on which had been deposited benzaldehyde (40%). Since the oxidation of benzaldehyde is catalysed by traces of heavy metals, the brick had first been impregnated with a solution of copper sulphate (0.1%). The benzaldehyde had been applied to the brick from acetone solution in an atmosphere of nitrogen freed from oxygen. The standard mixture comprised ethane, propene, but-1-ene, and but-2-ene, since these compounds were characterised by different retention times on benzaldehyde and benzoic acid. The procedure consisted in obtaining chromatograms of the standard mixture on the reaction mixture (benzaldehyde + benzoic acid) after definite intervals of time. The retention times of the compounds changed as the benzaldehyde was oxidised.

Chromatograms obtained on the original benzaldehyde and on the completely oxidised compound show (Fig. 6) a marked change in the retention times. At 0°C the concentration of benzoic acid in benzaldehyde corresponding to saturation is 7%, so that the composition of the liquid phase then remains practically constant during the oxidation, while the quantity of benzaldehyde (stationary liquid phase) decreases. During oxidation the corrected retention times vary in direct proportion to the content of benzaldehyde in the column. Therefore Eqn. (31) can be used in processing the experimental results, on the assumption that the kinetics of the oxidation of benzaldehyde to benzoic acid in the presence of oxygen corresponds formally to a first-order equation. The effective rate constant calculated by means of Eqn. (31) is 4.7×10^{-3} min^{-1}.

The results of the proposed method for studying the kinetics of the oxidation of benzaldehyde have been compared with those obtained by oxidation in a bubbler reaction vessel. These gave an oxidation rate constant of 4.6×10^{-3} min^{-1}. Thus the proposed chromatographic method of studying reaction kinetics gives results in good agreement with those obtained by a method of bulk oxidation.

The method under discussion can be applied not only to binary systems: in the case of multicomponent systems it is possible to select volatile compounds whose retention times would be greatly dependent on the content of individual components in the liquid phase.

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In conclusion we may note that the development of pulse gas-chromatographic methods is far from complete. An especially interesting application, it seems to us, is their development for study of the mechanism of liquid-phase reactions and of the effect of the medium on the rates of chemical changes. However, the experience which has now accumulated is sufficient for the wide application of pulse methods in the practical investigation of various liquid-phase reactions.

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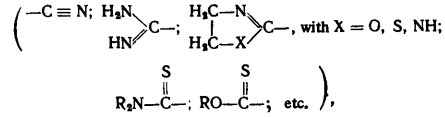
Rearrangements Connected with the Migration of Acyl and Certain Other Groups

L.V.Pavlova and F.Yu.Rachinskii

This review surveys instances of the migration of groups sensitive to nucleophilic attack (structures exhibiting the C=O, C=S, or C= N bonds) between two nucleophilic groups (NH_2, OH, and SH). Intramolecular rearrangements connected with the migration of acyl groups in acylated amino-phenols, amino-alcohols, polyhydric alcohols and phenols, diamines, thioglycols, amino-thiophenols, and amino-thiols are considered. The rearrangements take place by a common mechanism through the stage of formation of unstable cyclic compounds. Apart from the migration of acyl residues, instances of the rearrangements associated with migration of other groups which proceed by an analogous mechanism are surveyed in the article. Such rearrangements



are not only of theoretical interest but are also of great importance for preparative practice.

CONTENTS

I.	Introduction	587
II.	Migration of an acyl group in acylated amino-phenols and amino-alcohols	588
III.	Migration of an acyl group in acylated diamines	592
IV.	Migration of an acyl group in acylated polyhydric alcohols and phenols.	592
V.	Migration of an acyl group in acylated thioglycols and thioglycerols	593
VI.	Migration of an acyl group in acylated amino-thiophenols and amino-thiols	594
VII.	Rearrangment of aminoalkyl derivatives of isothiourea and isoselenourea	596
VIII.	Rearrangment of certain aminoalkyl sulphides	597

I. INTRODUCTION

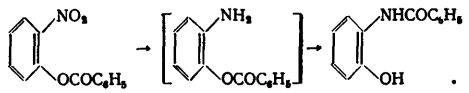
As long ago as the start of the XXth century several investigators observed examples of intramolecular rearrangements connected with the migration of acyl groups from an oxygen atom to a nitrogen atom in acylated amino-phenols; from oxygen at a secondary carbon atom to oxygen at a primary carbon atom in acyl derivatives of polyhydric alcohols, etc. Instances of N ⇌ O and S → N migrations of acyl groups in acylated amino-alcohols and amino-thiols are especially frequent. It was found later that migration between two nucleophilic groups (H_2N, OH, SH) is undergone not just by acyl but also by other groups sensitive to nucleophilic attack.

Such rearrangements are not just of theoretical interest as their mechanism is still not completely clear; they are also of great practical importance. In several instances these rearrangements formed the basis of the development of simple methods of synthesising complicated compounds, particularly *N*-substituted amino-thiols, guanidinoalkanthiols, and other compounds.

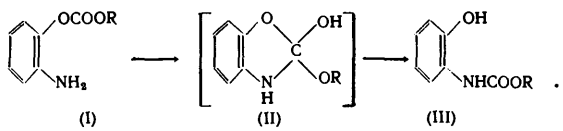
In this connection we thought it desirable to summarise the published data, both our own and those of other authors, assuming that a review of the intramolecular migration of acyl and other groups could prove useful for organic chemists.

II. MIGRATION OF AN ACYL GROUP IN ACYLATED AMINO-PHENOLS AND AMINO-ALCOHOLS

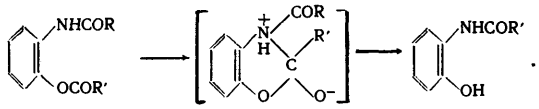
The investigations of Böttcher[1], Einhorn[2], and Auwers[3-5] showed that esters of *o*-amino-phenols and *o*-hydroxybenzylamines are very unstable and immediately after their formation they rearrange into the corresponding amides as a result of the migration of the acyl group from the oxygen atom to the nitrogen atom. Thus, in the reduction of *o*-nitrophenyl benzoate *N*-benzoyl-*o*-aminophenol was obtained as a result of the O → N rearrangement[1,3]:



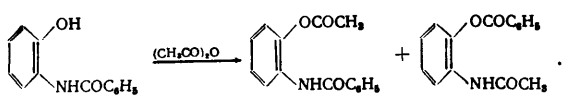
The analogous O → N migration of the alkoxycarbonyl group was observed in an example of the conversion of the *o*-aminophenyl alkyl carbonates (I) into the *o*-hydroxyphenylurethanes (III). The latter are obtained either in the reduction of *o*-nitrophenyl alkyl carbonates[6-8] or when aqueous solutions of the hydrochlorides of *o*-aminophenyl alkyl carbonates are kept for a long time[6-9]. It is suggested[6,8] that the rearrangement of (I) into (III) proceeds through the stage of the formation of an unstable cyclic compound (II):



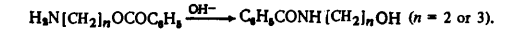
The migration of acid residues from oxygen to nitrogen also takes place in the partial hydrolysis of *ON*-diacyl derivatives of *o*-amino-phenols[10-14]. Probably here also the rearrangement proceeds through the stage of formation of an intermediate ring[14]:



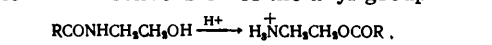
Moreover, examples are known of intramolecular migrations of acyl groups from a nitrogen atom to an oxygen atom for acylated *N*-alkoxycarbonyls[15-17] and *N*-acyl derivatives[11,18-30] of *o*-amino-phenol. For example, in the acylation of *N*-benzoyl-*o*-aminophenol with acetic anhydride as a result of the N → O migration of acyl groups a mixture of diacyl derivatives was isolated[31]:



Rearrangements connected with the migration of acyl groups were also observed in a series of derivatives of aliphatic amino-alcohols[32-54]. It was found that in an alkaline medium aminoalkyl benzoates are converted into hydroxyalkylamides[33]:

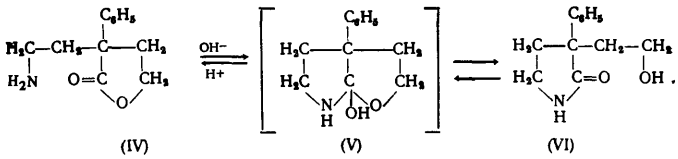


In an acid medium hydroxyalkylamides are in turn converted into *O*-acyl derivatives of amino-alcohols[33-38] as a result of the N → O conversion of the acyl group:

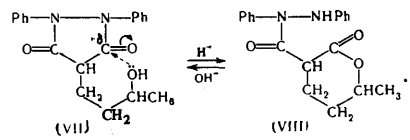


The reversibility of the migration of the acyl group (O ⇌ N) was also observed in the acyl derivatives of 2-amino-1-(naphth-2-yl)ethanol[45], 2-amino-1-phenylpropanol[40], and certain other amino-alcohols[46-54].

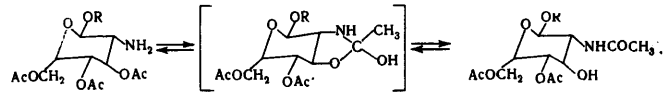
Walton and Green[55] consider that a similar reversible N ⇌ O migration of an acyl group also occurs in the example which they studied of the mutual conversion of 2-(2-aminoethyl)-2-phenyl-γ-butyrolactone (IV) into 3-(2-hydroxyethyl)-3-phenyl-2-pyrrolidone (VI). The authors assume that the formation of the intermediate cyclic compound (V) is possible:



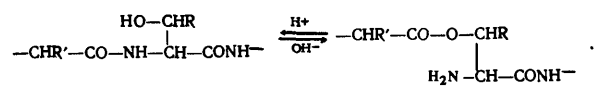
An analogous reversible N ⇌ O rearrangement was observed[56] in the conversion of pyrazolidinediones (VII) into lactones (VIII):



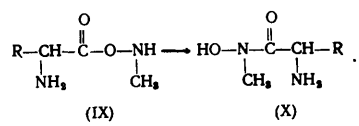
Instances of the N → O and O → N migration of acyl groups were also observed in a series of amino-sugar derivatives[57-63]:



The rearrangements connected with N → O and O → N migrations of the acyl groups were also observed in the residues of serine, threonine, and other amino-acids of proteins[62-85], the usual *N*-peptide bond being converted into an *O*-peptide bond:

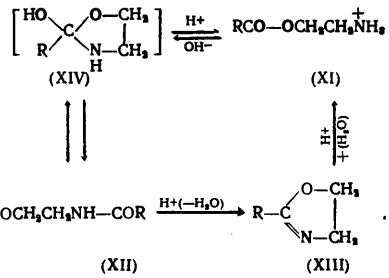


Probably such an O → N migration of an acyl group also occurs in the conversion of the hydrochloride of *O*-(2-aminoacyl)-*N*-methylhydroxylamine (IX) into the corresponding hydroxamic acid (X) when the solution is heated or left to stand for a long time[86]:



Phillips and Baltzly[87] give, as a possible mechanism of the migration of acyl groups, a scheme for the reversible

conversion of aminoalkyl esters (XI) into hydroxyalkylamides (XII):



These authors think that the oxazoline (XIII) is an intermediate in the N → O migration of an acyl group in a strongly acid medium. This is quite probable, since on the one hand oxazolines are formed[88-91] from hydroxyalkylamides (XII) and on the other hand they are readily converted[92-94] into salts of amino-esters (XI) in an acid medium.

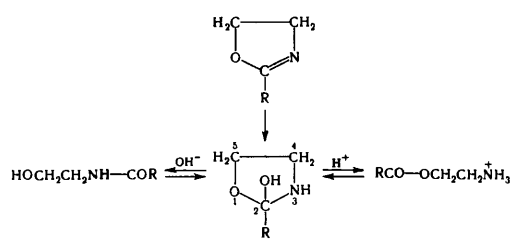
Phillips and Baltzly[87] succeeded in separating and identifying the oxazoline (XIII) in the rearrangement of the hydroxyamide (XII) into the amino-ester (XI). However, they think that the oxazoline (XIII), which is relatively stable in an alkaline medium, cannot be the intermediate cyclic compound in the O → N migration of an acyl group—a process which is observable only in an alkaline medium. This circumstance served as the basis for assuming that in an alkaline medium the change of (XI) into (XII) proceeds through the intermediate hydroxyoxazolidine (XIV) whereas in acid the conversion of (XII) into (XI) proceeds through the oxazoline[35,36,87], which was subsequently confirmed by kinetic studies of Porter and coworkers[95].

These authors found that for partly neutralised solutions of 2-methyloxazoline (XIII; R = CH_3), initially (XIII) is converted into an amino-ester (XI), which is, in turn, gradually converted into the hydroxyamide (XII). If it is assumed that the conversion of *O*-acetylethanolamine (XI; R = CH_3) into an *N*-acetyl derivative (XII; R = CH_3) proceeds through an oxazoline (XI) ⇌ (XIII) ⇌ (XII), then the *O*-acetylethanolamine (XI) can accumulate in the system.

On comparing the rate constants of these conversions it was found that the *N*-acetylethanolamine (XII) is formed more rapidly from the *O*-acetyl derivative (XI) than the latter from the oxazoline (XIII). The results obtained show that (XIII) cannot be an intermediate in the conversion of (XI) into (XII).

Kinetic investigations of similar acyl migrations carried out by other investigators[96-98] showed that the intermediate in both the O → N and the N → O migrations of acyl groups is hydroxyoxazolidine (XIV).

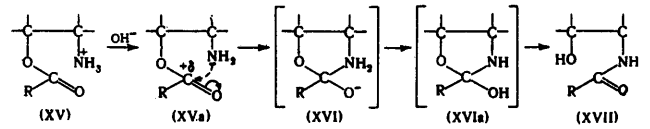
This conclusion agrees with the works of the study of the opening of the oxazoline ring[96,99,100]. Under the action of acid reagents the latter forms an amino-ester, and under the action of alkaline reagents, a hydroxy-amide. Furthermore, the breaking of the oxazoline ring is accompanied by the intermediate formation of a hydroxyoxazolidine, and the hydroxyl group in position 2 can lose a proton with opening of the ring in either the 1–2 or the 2–3 positions:



In an acid medium the bond in the 2–3 position is broken, owing to the C–N bond being more readily polarised than the C–O bond. On the other hand, in neutral or alkaline media the ring is broken in position 1–2 since the C–O bond is then more polarisable.

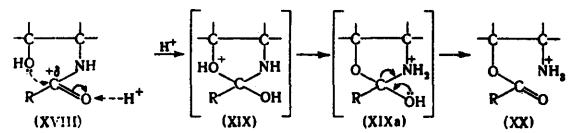
Phillips and Baltzly[87] mainly consider the structure of the intermediate cyclic compounds in reversible N ⇌ O migrations of the acyl groups. This served as a reason for other authors to express their hypotheses about possible mechanisms of such migrations.

Welsh[101,102] and Fodor and Kiss[103] consider that for the O → N migration of acyl groups the mechanism of the rearrangement can be represented by the scheme:



On the carbon atom of the carbonyl group of the amino-ester (XV) there is a certain positive charge as a result of the displacement of the electron cloud in the direction towards the oxygen atom of the carbonyl group, which exhibits a great affinity for the electron. Under the influence of hydroxyl ions (an alkaline medium) the salt of the amino-ester is converted into a base and the unshared electron pair of the nitrogen atom attacks the electron deficient carbonyl group, as a result of which a cyclic intermediate compound (XVI) is formed. The migration of a proton from nitrogen to the carbonyl oxygen gives structure (XVIa), in which as a result of alkaline hydrolysis the ester bond is broken and the hydroxyamide (XVII) is formed.

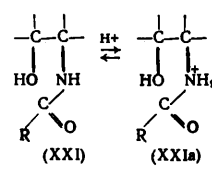
For the N → O migration of an acyl group the mechanism of the rearrangement can, according to Welsh[101,102], be represented by the scheme:



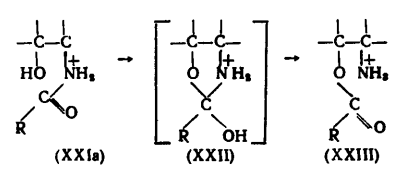
According to this scheme a proton is added to the carbonyl oxygen of compound (XVIII) and the intermediate unstable cyclic compounds (XIX) and (XIXa) are formed owing to interaction of the protonated carbonyl group with the alcoholic hydroxyl.

An analogous mechanism was almost simultaneously advanced to explain the migration of acyl groups in the formation of a mixture of *NO*-diacyl derivatives of *o*-aminophenol[31].

A somewhat different mechanism for the N → O migration of acyl groups, according to which the movement of the acyl groups takes place in two stages, was proposed by Fodor and Kiss[104]:



(1)



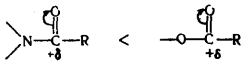
(2)

The first stage is the formation in a strongly acidic medium of the unstable salt of an *N*-acylamide (XXIa). The second stage is the formation of an intermediate cyclic compound (XXII), which then is stabilised by the breaking of the C–N bond owing to its greater polarisability in an acid medium with formation of a salt of an *O*-acylhydroxyamine (XXIII).

Starting from the above ideas on the possible mechanism of the N → O migration of acyl groups, it can be concluded that the rate of this rearrangement should increase with the hydrogen ion concentration. This was confirmed experimentally by Fodor and Kiss[105].

The influence of the pH of the medium on the degree of the O → N migration of an acyl group was also studied. It appeared that the degree of conversion of *O*-acyl derivatives of amino-alcohols into *N*-acyl derivatives increases with the pH of the medium[87,95,101,102,106]. For example, the conversion of 2-aminoethyl benzoate into an amide is complete at pH ~ 10; at pH 8 the degree of conversion reaches 20%, whereas at pH ≤ 7.5 the formation of the amide is hardly observed. A study of the reaction kinetics of the conversion of *O*-acetylethanolamine into the corresponding amide confirmed that with increase in the pH of the medium the rate of the rearrangement also increases[95].

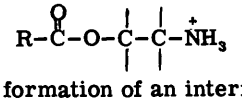
A noteworthy feature is that the N → O migration of an acyl group takes place only partly and at a low rate, whereas the O → N migration is instantaneous and almost quantitative[87,107,108]. This is evidently connected with the difference in the electronegativities of nitrogen and oxygen. As the electronegativity of nitrogen is less than that of oxygen the positive charge (+δ) on the carbon atom of the carbonyl group bonded with a nitrogen atom will be less than for a carbonyl group bonded with an oxygen atom:



This can probably explain why the rate of formation of an intermediate cyclic compound during the rearrangement of an *O*-acyl derivative of an amino-alcohol is greater than for the rearrangement of an *N*-acyl derivative.

Taking into account that the approach of a proton to oxygen or of a hydroxide ion to a carbonyl-carbon increases the electron displacement, it could be expected that the N → O and O → N migrations of an acyl group in acylated amino-alcohols will take place in both acid and alkaline media. However, the experimental results show that O → N migration takes place only in an alkaline medium and the N → O migration in acid, which agrees with the above mechanism of O ⇌ N migration[88,98,101–105], which assumes the formation of an intermediate cyclic compound.

The migration of an acyl group from oxygen to nitrogen in acylated amino-alcohols takes place only in an alkaline medium, since in an acid medium the amino-group exists in the form of the ammonium ion:



and therefore the formation of an intermediate ring is impossible.

With an *N*-acyl derivative of an amino-alcohol the N → O migration in an alkaline medium cannot proceed, since under these conditions the free electron pair of the nitrogen atom probably removes the positive charge on the carbon atom of the carbonyl group, making impossible the formation of an intermediate cyclic compound. This explains the stability of the hydroxyamides in an alkaline medium and of the amino-esters in acid.

The formation of an intermediate ring in N ⇌ O rearrangements is confirmed also by experimental results on the effect on this process of the mutual arrangement of the hydroxy- and amino-groups in the acylated amino-alcohols. Thus, N → O migration of an acetyl group is observed in the benzoylation of *o*-*N*-acetylaminophenol but is not observed for the *p*-isomer[29]; O → N migrations of the acyl group in acylated amino-alcohols of the general formula $RCOO[CH_2]_nNH_2$ only take place when $n = 2$ or 3, that is, under conditions when the closing of five- or six-membered rings is possible[33].

The migration of an acyl group in acyl derivatives of 1,2-amino-alcohols is also considerably affected by substituents at the carbon atoms[103,106–120].

For the acyl derivatives of the amino-alcohols $H_2N–CHR–CHR'–OH$, where R = R' = H, the free rotation around a C–C bond is not reflected on the acyl migration, but on introducing substituents which restrict free rotation the migration is naturally hindered and made more complicated.

In the acylated diastereoisomers of 1,2-amino-alcohols (*cis*- and *threo*-, *trans*- and *erythro*-) one observes the same rate of migration of acyl groups. As might have been expected, the similarity in the position of the functional groups (NH_2 and OH) should facilitate the formation of an intermediate ring, and consequently, a more rapid migration of acyl groups, which found confirmation in a series of studies[106–120].

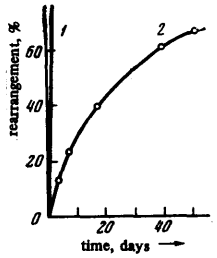
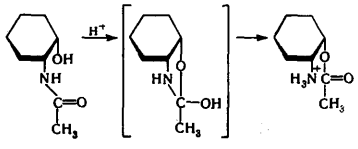
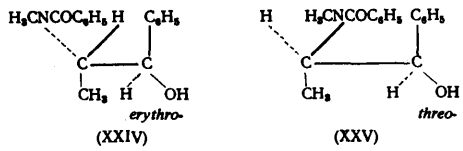


Figure 1. Rate of N → O rearrangement in 0.115 *N* alcoholic HCl solution:
1) *N*-benzoyl-ψ-ephedrine; *2*) *N*-benzoylephedrine.

For example, the rate of N → O migration of an acyl group in the *cis*- and *trans*-forms of *dl*-acetamidocyclohexanol are different; the *cis*-form rearranges 5–6 times more rapidly than the *trans*-form[114]:



It was also shown that the rate of the N → O migration of the benzoyl group in *N*-benzoylephedrine (XXIV) and *N*-benzoyl-ψ-ephedrine (XXV) differ considerably under the same conditions[101,107], as Fig. 1 shows.



The examples given above show that unlike the rapid migration of acyl groups in acylated 1,2-amino-alcohols having *cis*- and *threo*-forms in the analogous compounds of *trans*- and *erythro*-forms the rearrangement is extremely slow[111-116] and is accelerated only on raising the temperature[104,105]. Thus, the *N*-benzoyl derivative of *trans*-aminocyclohexanol undergoes hardly any rearrangement at room temperature, whereas in a sealed tube at 100°C an *O*-benzoyl derivative is formed in 48–50% yield after 2 h.

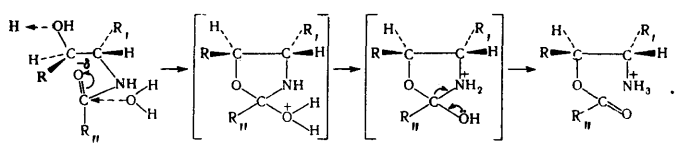
By making use of the difference in the rate of migration of acyl groups in diastereoisomers, the configuration of amino-alcohols can be established[101-116,121-126].

To separate the stereoisomers, Fodor proposed[110,111,115] to treat a mixture of the *N*-acyl derivatives of *threo*- and *erythro*-forms of amino-alcohols with hydrochloric acid at room temperature. Here the *N*-derivatives of the *threo*-forms are rapidly and almost quantitatively rearranged into *O*-derivatives as a result of the N → O migration of acyl groups, whereas the *N*-derivatives of the *erythro*-forms are unchanged under these conditions. The *O*-acyl derivatives of the *threo*-forms which are produced are readily soluble in aqueous hydrochloric acid and hence are easily separated from the *N*-acyl derivatives of the *erythro*-forms.

Fodor also noted[110] that the prolonged holding of *N*-benzoylephedrine (*erythro*-form) in alcoholic HCl brings about its partial conversion into *O*-benzoyl-ψ-ephedrine (*threo*-form). An analogous change in the configuration as a result of the migration of acyl groups was also observed by Welsh[101,102] on treating *N*-acyl-ψ-ephedrine with hot alcoholic HCl; only *O*-acyl-ψ-ephedrine is obtained, whereas the products of the acyl migration of *N*-acetylephedrine are the *O*-acetylephedrine and a large proportion of *O*-acetyl-ψ-ephedrine. It appears that the migration of an acyl group can proceed in two directions: with retention of the configuration of the amino-alcohol (*R*-mechanism) and with change in configuration (*I*-mechanism).

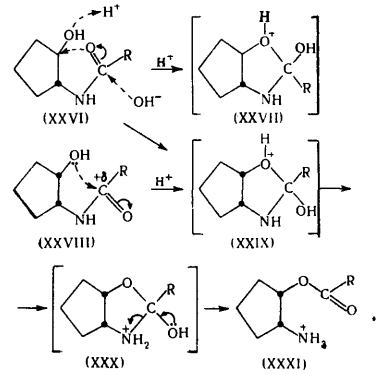
The migration of an acyl group (N → O) in acylated 1,2-amino-alcohols with a linear structure usually proceeds with retention of the configuration[103,104,109,114,115] and only in exceptional instances and severe experimental conditions is the rearrangement accompanied by a change in configuration[101,102,105,110,113,114].

The *I* mechanism of the rearrangement can be represented by the scheme[101,102]:



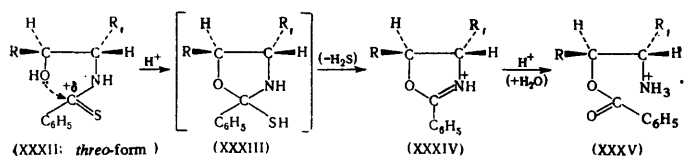
According to this scheme complete inversion at the carbon takes place as a result of the approach of the carbonyl oxygen to the asymmetric carbon atom simultaneously with the attack by the proton at the hydroxyl oxygen.

The migration of an acyl group (N → O) with inversion is observed also in a series of acylated alicyclic amino-alcohols[121]. Thus under the action of hydrogen chloride *cis*-*N*-acetylated amino-alcohols are converted into *cis*-*O*-acetyl derivatives, whereas the *trans*-derivatives are not rearranged under these conditions. However, under severe conditions (boiling, long treatment with HCl) *trans*-*N*-acetyl derivatives are converted into *cis*-*O*-acetyl derivatives, but the rearrangement is accompanied by a change in configuration:



In the *cis*-isomer (XXVIII) the N → O migration of an acyl group takes place readily, since the intermediate compound (XXIX) is formed without strain. In the *trans*-isomer (XXVI) rearrangement with retention of configuration is prevented by steric factors. The intermediate compound (XXVII) is structurally strained and is obtained from the amide of the *trans*-isomer (XXVI) with great difficulty, therefore the migration of an acyl group leading to the *trans*-ester is very difficult. Although in compound (XXVI) in the N → O migration of an acyl group the removal of a hydroxyl after the scheme of the *I* mechanism requires more severe conditions the formation of the intermediate compound (XXIX) may be more rapid than that of (XXVII).

As confirmation of the proposed mechanisms of N → O migration of an acyl group both with retention of the configuration and with inversion there is the work on the replacement of an acyl group by a thioacyl[127]. For the *threo*-epimers of *N*-thiobenzoyl derivatives of amino-alcohols studied by Farkaš and Sicher[127] the replacement of the acyl group as might have been expected, proceeds by the *R* mechanism:

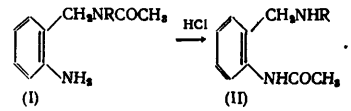


2-Mercapto-2-phenyloxazolidine (XXXIII) is formed as the intermediate cyclic compound and is stabilised in the form of 2-phenyloxazoline (XXXIV) which is readily converted in an acid medium into an amino-ester salt (XXXV). Therefore on heating with alcoholic HCl the *N*-thiobenzoyl derivatives of *threo*-isomers of 1,2-amino-alcohols were isolated as the hydrochlorides of amino-esters; the formation of aminothioesters was not observed.

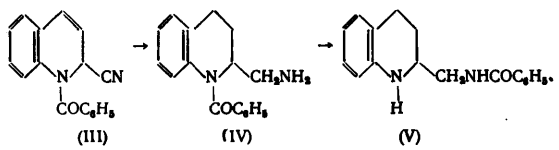
As already reported for *erythro*-epimers N → O migration of acyl groups can take place by either an *R* mechanism or with inversion (*I* mechanism). It is known[88,101,102,128,129] that the *I* mechanism presumes nucleophilic attack of the oxygen atom of the carbonyl group at the β-carbon atom. Since sulphur is more nucleophilic than oxygen the replacement of an acyl group by thioacyl should facilitate for *erythro*-epimers the reaction by an *I* mechanism, which was also confirmed in the study by Farkaš and Sicher[127].

III. MIGRATION OF AN ACYL GROUP IN ACYLATED DIAMINES

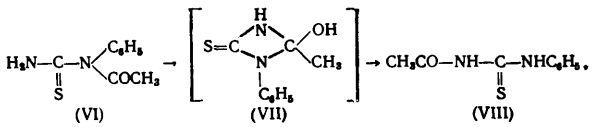
At the end of the last century Widman[130] noted that the 2-acetamidomethylaniline (I) is converted into 2'-(aminomethyl)acetanilide (II) on treatment with hydrochloric acid:



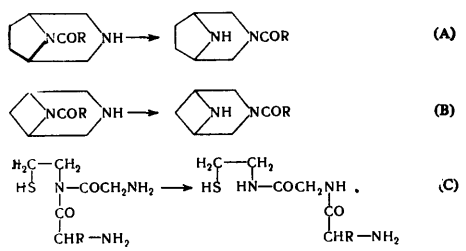
The analogous N → N' migration of the acyl group was also observed in the reduction of 1-benzoyl-2-cyano-1,2-dihydroquinoline (III). As a result of the reaction 2-(benzamidomethyl)tetrahydroquinoline (V) was isolated. The authors[131-133] suggested that initially 2-aminomethyl-1-benzoyltetrahydroquinoline (IV) is formed, which then undergoes rearrangement accompanied by the N → N' migration of an acyl group:



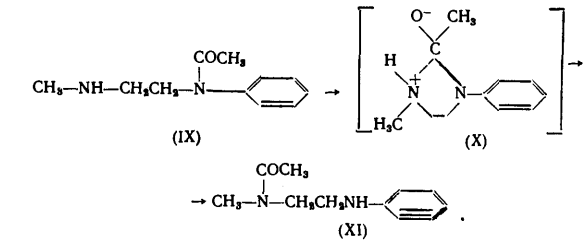
The rearrangement described by Wheeler[134] of the unsymmetrical *N*-acyl derivatives of thiourea (VI) in isomeric symmetrical derivatives (VIII) is also probably connected with the N → N' migration of acyl groups taking place through the stage of formation of an intermediate unstable ring (VII):



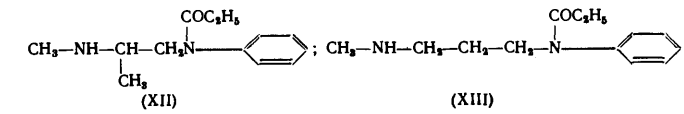
Subsequently an example of the N → N' migration of acyl groups was observed in the derivatives of ethylenediamine[135], triazines[136], aminoalkylanilines[137], 3,8-diazabicyclo[3,2,1]octane (A),[138] 3,9-diaza-bicyclo[3,3,1]nonane (B),[139] and also *N*-aminoacylated amino-thiols (C):[140-142]



It was suggested[137-142] that the N → N' migration of acyl groups proceeds by a mechanism similar to the analogous N → O migration in acylated amino-alcohols. Thus *N*-(2-anilinoethyl)-*N*-methylacetamide (XI) was isolated from the distillation of *N*-(2-methylaminoethyl)acetanilide (IX). In the opinion of Wright and coworkers[137] (XI) is obtained as a result of the intramolecular rearrangement of (IX), which passes through the stage of formation of the unstable intermediate five-membered ring (X):



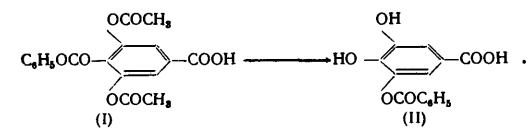
As was shown[137], the rate of rearrangement depends on the structure of the initial compounds, which confirms the mechanism of the N → N' migration through a stage of formation of an intermediate ring. Compound (IX), which contains two methylene groups between nitrogen atoms, rearranges readily on distillation (90–130°C). *N*-(2-Methylaminopropyl)propioanilide (XII) is more stable and on distillation is rearranged to only a slight extent, but the rate of rearrangement is considerably increased at 175–185°C. This fact can probably be explained by steric hindrance in the formation of an intermediate ring. *N*-(3-Methylaminopropyl)propionanilide (XIII), in which the N → N' migration of an acyl group should take place through the stage of formation of an intermediate six-membered ring, is fairly stable and is only partly rearranged at temperatures > 200°C:



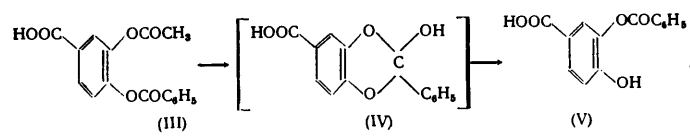
IV. MIGRATION OF AN ACYL GROUP IN ACYLATED POLYHYDRIC ALCOHOLS AND PHENOLS

The migration of acyl groups has also been noted in a series of acylated polyhydric phenols and alcohols.

Thus, in the hydrolysis of 3,5-diacetyl-4-benzoylgallic acid (I), both in acid and in aqueous solutions of weak bases, 3-benzoylgallic acid (II) is formed[143]:

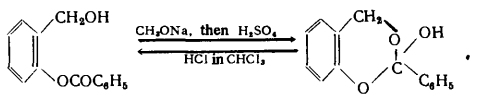


In the treatment of 3-acetyl-4-benzoylprotocatechuic acid (III) with bases or acids, 3-benzoylprotocatechuic acid (V) was isolated[144]. Fischer[144] thinks that this O → O' migration of an acyl group proceeds through the intermediate cyclic compound (IV):



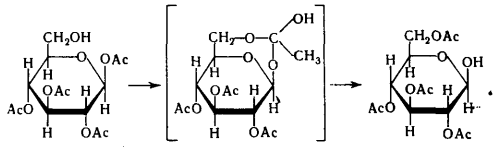
The possibility of the existence of an intermediate cyclic compound of type (IV) was shown by Helferich and Liesen[145]

by the example of 2-benzoyloxybenzyl alcohol (benzoylsaligenin), which was isolated in two desmotropic forms—open (VI) and cyclic (VII), capable of mutual interconversion:



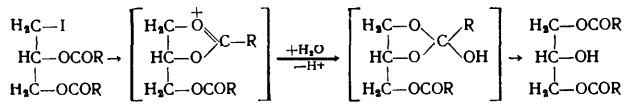
(VI) (VII)

The migration of acid residues (O → O′) is also observed for acyl derivatives of glucose[146-154]. In the given example the rearrangement proceeds through the stage of formation of an intermediate ring[152-154]:



A similar O → O′ rearrangement of acyl groups was observed in the preparation of mixed esters of glycerol[155] and in the saponification of triglycerides[156]. For example, in the action of silver nitrite on alcoholic solutions of αβ-di-(*p*-nitrobenzoyl)-α′-iodohydrin or αβ-distearyl-α′-iodohydrin with the aim of obtaining diesters of glycerol containing a free alcoholic group in the α′-position αα′-di-(*p*-nitrobenzoyl)- and αα′-distearyl-glycerols with a free hydroxyl group in the β position were isolated.

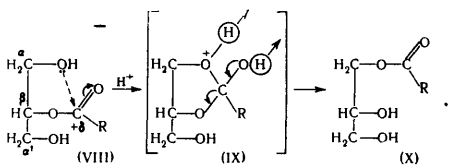
In these instances, according to Winstein and Buckles[157] migration of an acyl group also proceeds through intermediate cyclic compounds:



where R = *p*-$NO_2C_6H_4$, $C_{17}H_{35}$.

According to Fischer[143,144,155], the mechanism of migration of acyl groups in polyhydric alcohols is connected with the intramolecular interaction of and OH groups with the formation of an intermediate cyclic compound, which then opens with the migration of a hydrogen atom.

The mechanism of the O → O′ migration of acyl groups in polyhydric alcohols was considered in greater detail by Doerschuk[158], who proposed the following scheme:



(VIII) (IX) (X)

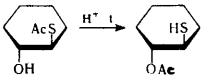
For the carbonyl group the partial shift of an electron pair to the side of the more electronegative oxygen atom and the consequent appearance of some positive charge on the carbon atom of the carbonyl group is characteristic. The electron pair of the oxygen atom of the hydroxyl group attacks the electron deficient carbonyl group (VIII); during this an intermediate cyclic compound (IX) is formed which is cleaved at the C–O bond in the β-position owing to its easier polarisability, forming (X).

On assuming such a mechanism for the O → O′ migration of an acyl group the rate of rearrangement should be influenced by the degree of polarisation of the carbonyl group and consequently also the magnitude of the positive charge on the carbonyl carbon, which is due to the influence of the pH of the medium and the nature of the acyl group. In experiment this in fact was confirmed[159,160]. For example, glyceryl β-monopalmitate in alcoholic 0.5 *N* HCl at room temperature is completely converted into the α-isomer in 24 h, whereas in more dilute solutions (0.005 *N*) rearrangement does not take place[159]. The benzoyl group migrates slowly[158] or not at all[160] owing to the effect of conjugation, leading to some filling of the electron deficiency on the carbonyl carbon. On the other hand, the rearrangement proceeds rapidly for the acetyl group. This is especially noticeable for the example of the β-trichloroacetyl group with a clearly expressed positive charge on the carbonyl-carbon[156].

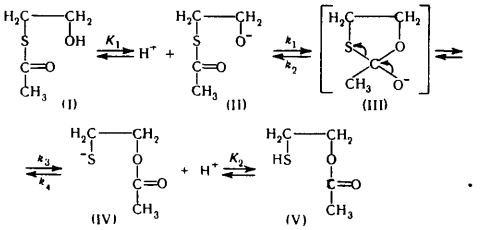
Proof of the intramolecular mechanism of the O → O′ migration of the acyl group was given by the results[158] on the rearrangement of glyceryl β-monopalmitate in an acid medium in the presence of labelled 1-^{14}C glycerol. As a result of this reaction α-monopalmitate free from ^{14}C was isolated.

V. MIGRATION OF AN ACYL GROUP IN ACYLATED THIOGLYCOLS AND THIOGLYCEROLS

In thioglycols[161-166] and thioglycerols[167] the S → O migration of an acyl group is observed in neutral and alkaline media, and under severe conditions also in an acid medium[168]. For example, on long heating in an acid medium *trans*-2-acetylthiocyclohexanol is converted into *trans*-O-acetyl-2-thiocyclohexanol:



As a result of Martin and Hedrick's investigations[166] it is suggested that the S → O migration of acyl groups can be represented by the scheme:



(I) (II) (III) (IV) (V)

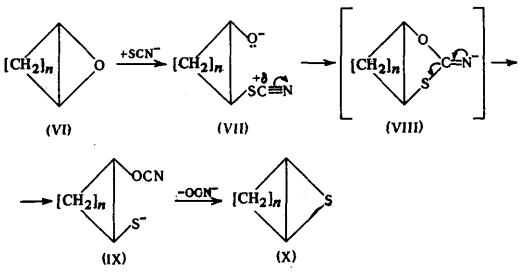
where K_1 and K_2 are the acid ionisation constants and k_1–k_4 the rate constants for cyclisation and breaking of the C–O and C–S bonds respectively.

As for the acyl derivatives of amino-alcohols[87,97,98] and polyhydric alcohols[155,157] the migration of acyl groups in acylated thioglycols proceeds through the formation of an unstable intermediate cyclic compound (III) which is opened at the site of the most easily polarisable bond, depending on the pH. It has been shown that the migration of an acyl group from sulphur to oxygen takes place only in neutral or alkaline media; the reversible O → S migration was not observed here. According to Martin[166], the stage of cyclisation precedes the ionisation of acyl derivatives of thioglycols with the formation of a thiolate ion (IV) or an alkoxide ion (II), which naturally is possible in alkaline or neutral media. The formation of a cyclic intermediate compound (III), as for O ⇌ N, N → N′, O → O′ migrations is also connected with the intramolecular interaction of a carbonyl carbon with a hydroxyl oxygen, in the example of (II), or with sulphur—for (IV). Since nucleophilic properties are

expressed more strongly by sulphur than by oxygen the formation of intermediate ring (III) from the thiolate ion (IV) should be faster than the formation of (III) from (II), which is confirmed by the ratio of the rates of these reactions ($k_1/k_4 = 1/20$). However, a study of reaction rates showed that the ratio $k_2/k_3 \simeq 10^{-10}$, that is, the rate of opening of ring (III) with the formation of the S-acyl derivative (I) is so low that the process proceeds in the main with the formation of the *O*-acyl derivative (V).

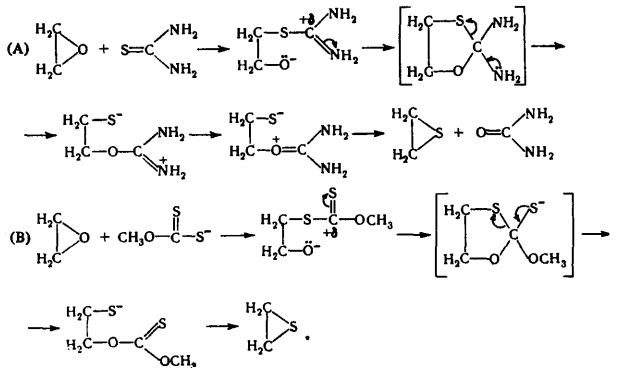
The migration of an acyl group was also studied in the $CH_3COS[CH_2]_nOH$ series where $n = 2, 3, 4$. As might be expected, in accordance with the assumption concerning the formation of an intermediate cyclic compound, the migration of acyl groups takes place rapidly for $n = 2$, more slowly for $n = 3$, and hardly at all at $n = 4$. It was found that the rate of the S → O migration in *S*-acetylmercaptoethanol is approximately 30 times as great as the rate of the analogous change in propyl compounds[165].

Intramolecular rearrangements can occur as a result of the S → O migration not only of acyl[161-166] but also of other groups. Thus the formation of alkylene sulphides (X) in the reaction of alkylene oxides (VI) with thiocyanates[163,169-173] is connected with the migration of CN groups from the sulphur atom to the oxygen atom:



The intermediate cyclic compound (VIII) was isolated[172] as a *p*-nitrobenzoyl derivative.

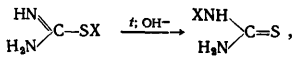
The formation of alkylene sulphides in the interaction of alkylene oxides with thiourea[169,174] or with methyl xanthates[174] must be considered as a reaction in which there is an S → O migration of amidine (A) or thiomethoxycarbonyl (B) groups:



VI. MIGRATION OF AN ACYL GROUP IN ACYLATED AMINO-THIOPHENOLS AND AMINO-THIOLS

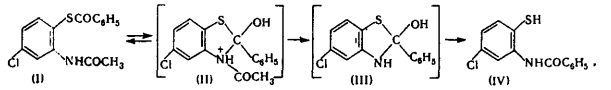
Rearrangements which are accompanied by the migration of acyl groups from a sulphur atom to a nitrogen atom were first observed for *S*-acyl derivatives of thiourea[175-178] and diacyl derivatives of *o*-amino-thiophenols[179].

It was noted that *S*-acyl[175-177] and *S*-alkoxycarbonyl derivatives[178] of thiourea are converted into the corresponding *N*-derivatives of thiourea on heating or basification:



where X = COR or COOR.

In the alkaline hydrolysis of 2-acetamido-4-chlorophenylthiobenzoate (I) 2-benzoylamino-4-chlorothiophenol (IV) was isolated and characterised. By analogy with the acyl migration in acylated amino-phenols[14] it can be assumed that here an S → N migration is accompanied by the formation of intermediate unstable cyclic compounds (II) and (III):



An analogous S → N migration of acyl groups in a series of aliphatic compounds containing sulphur and nitrogen, leading to *N*-substituted amino-alkanethiols was first reported by Baddiley and Thain[180] in 1951 by the example of *S*-acetylmercaptoethylamine; the latter gradually forms a thiol in aqueous solution. A freshly prepared solution of *S*-acetyl-2-mercaptoethylamine shows initially a negative reaction for the SH group but after as little as 5 min the proportion of SH groups becomes appreciable.

The formation of thiol can here be assumed to be the result of the following processes.

(a) Hydrolysis of the *S*-acyl derivative with the formation of an amino-thiol and an acid:

$$CH_3COSCH_2CH_2NH_2 + H_2O \rightarrow CH_3COOH + HSCH_2CH_2NH_2.$$

(b) Migration of the acyl group from the sulphur atom to the nitrogen atom, that is, as a result of "reacylation":

$$CH_3COSCH_2CH_2NH_2 \rightarrow HSCH_2CH_2NHCOCH_3.$$

Subsequent investigations cast light on the mechanism of conversion of an *S*-acyl derivative of 2-mercaptoethylamine.

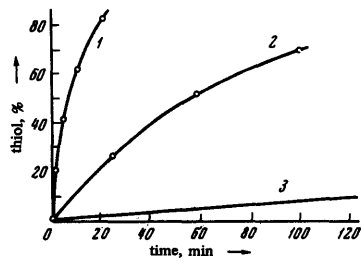
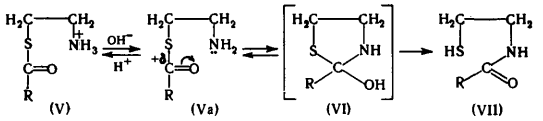


Figure 2. Rate of conversion of S-acetyl-2-mercaptoethylamine into a thiol as a function of the pH of the solution: *1*) pH 5; *2*) pH 4; *3*) 1 *N* HCl.

Wieland and Bokelmann[181] found that *S*-acetyl-2-mercaptoethylamine is extremely stable in 2 *N* HCl, and the formation of free thiol is not observed under these conditions. With decrease in the acidity of the solution (pH ≃ 4) the reaction at the SH group becomes positive and a gradual rise in thiol concentration is observed (Fig. 2). The main products of the conversion of *S*-acetyl-2-mercaptoethylamine in neutral and weakly acidic media were

N-acetyl-2-mercaptoethylamine and 2-methylthiazoline-Δ^2; 2-mercaptoethylamine, a possible hydrolysis product, was not observed even by a chromatographic method[181].

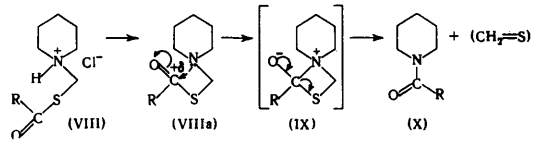
Experimental results[180-182] and kinetic studies[98,166,183,184] suggest that the conversion of *S*-acyl derivatives of amino-thiols (V) in neutral and weakly alkaline media proceeds as a result of an intramolecular S → N migration of an acyl group through the stage of formation of an intermediate cyclic compound (VI) according to the scheme:



(V) (Va) (VI) (VII)

In strongly acid media where the concentration of free amino-groups is insignificant owing to the formation of ammonium ions (V), the rate of this conversion should be low. With increase in pH the concentration of free amino-groups increases (Va), and consequently there is an increase in the rate of "reacylation".

The formation of an intermediate cyclic compound of the type of (VI) found confirmation in the studies of Smissman and Sorenson[185] and others[186]. Thus on distilling the free base 1-piperidinomethyl thioacetate (VIIIa), 1-acetylpiperidine (X) was obtained. The mechanism of this transformation can be represented as follows:



(VIII) (VIIIa) (IX) (X)

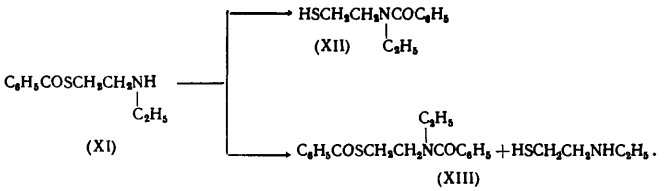
An investigation of the rate of "reacylation" of *S*-acetyl-2-mercaptoethylamine showed that at pH 4 and 5 the reaction is unimolecular[181] but at pH > 5 it becomes bimolecular[98,183,184]. However, it is difficult to explain such a marked change in the order of reaction for so slight a change in pH.

As well as the pH of the medium, the nature of the acyl group at the sulphur atom also affects the rate of migration of the acyl groups in amino-thiols, also in both the O → O′ and the O → N migrations. For example, *S*-benzoyl-2-mercaptoethylamine is converted into the thiol at one-tenth the rate of the conversion of the *S*-acetyl derivative[181].

Since the migration of acyl groups proceeds through the formation of an intermediate cyclic compound, it is quite natural for rearrangement to occur only for amino-thiols containing a primary or secondary amino-group. Compounds which contain a tertiary amino-group do not rearrange and in aqueous solution can only be hydrolysed with the formation of a free thiol. Thus *S*-acetyl-2-dimethylaminoethyl mercaptan undergoes partial hydrolysis at pH 7–8 and in 1 h forms ~ 17% SH groups titratable by iodine as a result of this[181].

In studying the migration of acyl groups in *S*-acetyl derivatives of amino-alkanethiols of general formula $CH_3COS[CH_2]_nNH_2$ (with $n = 3$, 4, 6, or 10), it was found that at pH ~ 7.0 apart from *S*-acetyl-2-mercaptoethylamine ($n = 2$), only *S*-acetyl-3-mercaptopropylamine ($n = 3$) is rearranged at a measurable rate[182]. On comparing the rate of reacylation of the β- and γ-*S*-acetyl derivatives of amino-thiols the γ derivative is rearranged at one-hundredth the rate of the β-substituted derivative. This agrees with the finding that the formation of an intermediate five-membered cyclic compound from the *S*-acetyl-2-mercaptoethylamine ($n = 2$) takes place 70 times more rapidly than the formation of the corresponding six-membered ring from *S*-acetyl-3-mercaptopropylamine[183]. The higher homologues of *S*-acetyl-ω-aminoalkanethiols ($n = 4$, 6, 10) cannot undergo rearrangement and their deacylation is possible only as a result of hydrolysis, the rate of which increases with the pH[182].

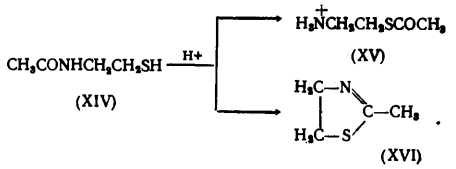
Certain other instances of S → N migration of acyl groups are also known. Thus in an attempt to isolate the free base of 2-ethylaminoethyl thiobenzoate (XI) from its hydrobromide, Stirling[187] obtained a product of S → N migration—*N*-benzoyl-2-ethylaminoethanethiol (XII); in addition to that an *NS*-dibenzoyl derivative (XIII) was also isolated from the reaction products; its formation can be explained by the reaction of the amido-thiol (XII), obtained as a result of S → N rearrangement, with the amino-ester (XI):



(XI) (XII) (XIII)

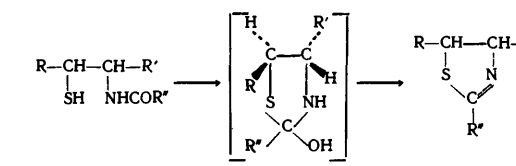
Rearrangements associated with the S → N migration of acyl and alkoxycarbonyl groups was also observed for *S*-derivatives of cysteine[188,189], peptides[190], ephedrine[191], and 2-mercaptoethylamine and acylated amino-acids[140-142,192,193].

It must be pointed out that very little information has been published on the N → S migration of acyl groups in an acid medium. Martin and coworkers[183] found that *N*-acetyl-2-mercaptoethylamine (XIV) in an acid medium forms mainly 2-methylthiazoline-Δ^2 (XVI), together with a little *S*-acetyl-2-mercaptoethylamine (XV), which was identified only spectrophotometrically:

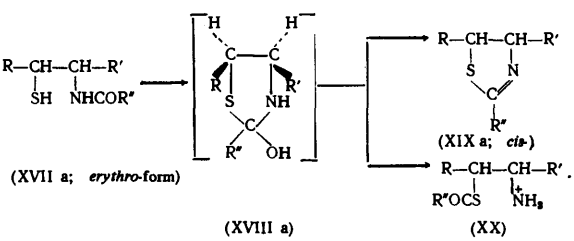


(XIV) (XV) (XVI)

An instance of N → S migration of an acyl group in an acid medium was also observed by Sicher and Svoboda[194,195] in studying the cyclisation of epimers of *N*-acyl derivatives of acyclic 1,2-amino-thiols (*threo*- and *erythro*-forms). The first stage of reaction for both epimers (XVII, XVIIa) is the formation of an unstable 2-hydroxythiazolidine intermediate derivative (XVIII, XVIIIa):



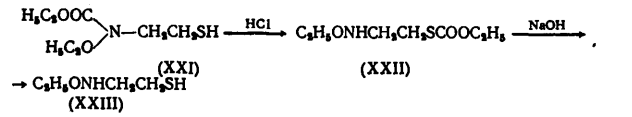
(XVII; *threo*-form) (XVIII) (XIX; *trans*-)



(XVII a; *erythro*-form) (XVIII a) (XIX a; *cis*-) (XX)

For the *threo*-epimer (XVII) the intermediate ring (XVIII) in an acid medium is converted exclusively into Δ^2-thiazoline derivative (XIX), where the substituents R and R' at the carbon atoms are in the *trans*-position, that is, the formation of (XIX) does not lead to approach of the substituents. For the *erythro*-epimer (XVIIa) the product of the N → S migration of the acyl group is formed–*S*-acylaminoalkanethiol (XX), since the formation of (XVIIIa) from (XVIIa) leads to the approach of the substituents R and R', and the thiazoline ring (XIXa) is structurally strained. As a result of this there is opening of the hydroxythiazolidine intermediate ring (XVIIIa) at the C–N bond, and the acyl group migrates from the nitrogen atom to the sulphur atom.

An example of an N → S migration of an ethoxycarbonyl group has also been described[196]. In the treatment of 2-(*N*-ethoxy-*N*-ethoxycarbonylamino)ethyl mercaptan (XXI) with dilute hydrochloric acid the formation of the thiol carbonate (XXII) was observed; this was then converted by alkaline hydrolysis into the thiol (XXIII):



From what has been said above it follows that the migration of acyl groups in acylated amino-alcohols and amino-thiols proceeds by a similar mechanism. In the first stage of the process, whether in acid or in alkaline media, an intermediate unstable cyclic compound (hydroxyoxazolidine) for amino-alcohols and hydroxythiazolidine for amino-thiols) is formed. In the second stage this intermediate cyclic compound is converted, depending on the pH of the medium, into various final products.

A comparative study of the rate of migration of acyl groups in acylated derivatives of amino-alcohols and amino-thiols showed that the rate of the S → N migration is greater than that of the O → N migration[97]. Moreover it is known that the formation of a hydroxyoxazolidine as an intermediate compound in the rearrangement of *O*-acyl derivatives of amino-alcohols takes place 140 times more rapidly than the formation of hydroxythiazolidine from amino-thiols[97].

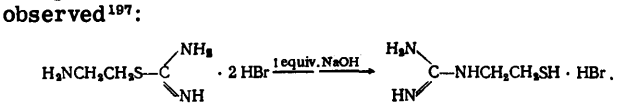
This is probably influenced by the fact that a positive charge on the carbon atom of the carbonyl group connected with the oxygen atom is greater than that at the carbon atom of a carbonyl group connected with a sulphur atom.

It can be suggested that owing to this effect the rate of O → N migration should be greater than the rate of S → N migration. But since the subsequent opening of the hydroxythiazolidine ring in an alkaline medium, leading to the formation of an *N*-acyl derivative of the amino-thiol takes place much more rapidly than the opening of the hydroxyoxazolidine[97], in the end the rate of the S → N rearrangement is greater.

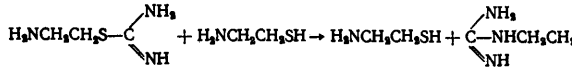
VII. REARRANGEMENT OF AMINOALKYL DERIVATIVES OF ISOTHIOUREA AND ISOSELENOUREA

Rearrangements similar to the S → N migration of acyl groups in acylated amino-thiols are also observed in a series of aminoalkyl substituted isothioureas[197–204].

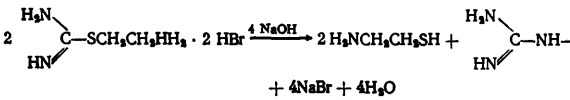
Thus during the neutralisation of an aqueous solution of a salt of *S*-2-aminoethylisothiourea with one equivalent of alkali (pH ≃ 7.0) the formation of 2-mercaptoethylguanidine is observed[197]:



Initially attempts were made to explain the mechanism of such a conversion by the known reactions for the aminolysis of *S*-substituted thioureas, leading to the formation of guanidine derivatives[205,206]:



But here the aminolysis should precede the hydrolytic splitting of the C–S bond in 2-aminoethylisothiourea with the formation of 2-mercaptoethylamine; this is possible only at pH > 10 and elevated temperature:

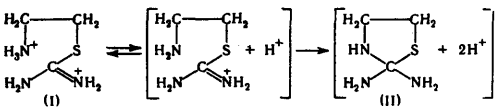


In studying the stability of aqueous solutions of *S*-2-aminoethylisothiourea at various pH, Khym and coworkers[199] found that this compound does not change at room temperature in 0.2 *N* HCl in 14 days. At pH ≃ 3.5, *S*-2-aminoethylisothiourea in aqueous solution is completely converted into 2-aminothiazoline and an ammonium salt after four days. At somewhat higher pH (~ 4.5) in addition to 2-aminothiazoline, 2-mercaptoethylguanidine is also observed. In neutral or weakly alkaline medium this isothiuronium compound is instantaneously and completely converted into 2-mercaptoethylguanidine. In a strongly alkaline medium the reaction for the formation of a guanidine derivative competes with the reaction for the formation of 2-mercaptoethylamine as a result of the hydrolytic splitting of the isothiuronium salt, and consequently both 2-mercaptoethylguanidine and 2-mercaptoethylamine are observed in the solution together.

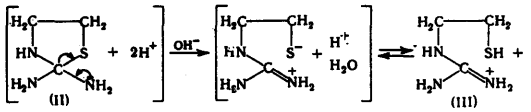
The above authors gave the name "transguanidation" to the conversion of the isothiouronium compounds into guanidine and thiazoline derivatives[199], as it is a special case of intramolecular S → N rearrangement.

The mechanism of this rearrangement is explained as follows: *S*-2-aminoethyl isothiourea (I) can exist in an unstable cyclic form (II) which is produced as a result of nucleophilic attack by the β-amino-group on the thiourea residue. This unstable intermediate cyclic compound (II) is subsequently converted either into 2-mercaptoethylguanidine (III) or into 2-aminothiazoline (IV), depending upon the reaction medium: according to the following scheme:

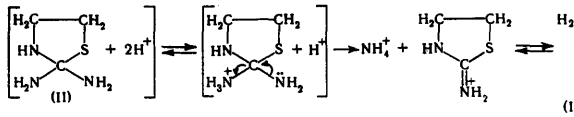
A. Formation of an unstable intermediate ring:



B. Stabilisation of intermediate ring (II) at pH ≃ 7.0:



C. Stabilisation of ring (II) at pH ≃ 3.5:



In neutral or weakly alkaline media cleavage of ring (II) occurs with formation of 2-mercaptoethylguanidine (III)

since at a low proton concentration the uncharged amino-group facilitates migration of the electrons of the neighbouring C–S bond to the sulphur atom, which in this way leads to breaking of this C–S bond and formation of (III).

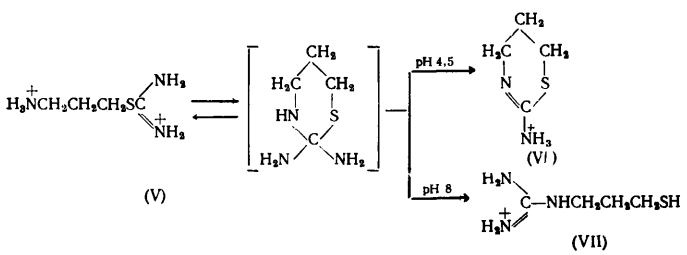
In a weakly acid medium as a result of addition of a proton to one of the amino-groups electrons of the C–N bond are displaced, an ammonium ion is lost, and 2-aminothiazoline (IV) is formed.

Confirmation of the "transguanidation" reaction scheme, which proceeds with formation of an intermediate cyclic compound, was also obtained by Rachinskii and Slavachevskaya[207], who studied the rate of conversion of *S*-2-aminoethylisothiuronium into 2-aminothiazoline in aqueous solution at pH ~ 3.5.

In addition the authors[207] showed that the reaction of "transguanidation" can be used to obtain a series of guanidinoalkanethiols and the corresponding disulphides.

In studying the behaviour of various *S*-substituted thioureas in aqueous solutions it was observed that in neutral or weakly alkaline media there is a sharp difference in the rate of formation of the thiol depending on the structure of the isothiuronium salts[207]. Aminoalkylisothiuronium compounds, which contain a primary or secondary amino-group in the β or γ position at pH ~ 7.5 are converted almost instantaneously and quantitatively into the thiol, whereas the analogous compounds with a tertiary amino-group do not form a thiol under these conditions.

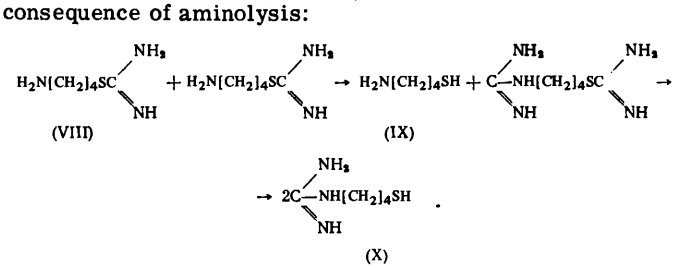
In addition it has been noted that *S*-3-aminopropylisothiourea (V) undergoes rearrangement at a higher pH than *S*-2-aminoethylisothiourea[201]. Thus the optimal conditions for the quantitative conversion of (V) into 2-aminopenthiazoline (VI) are pH 4.5 and for rearrangement into 3-mercaptopropylguanidine (VII), pH 8.



(V) (VI) (VII)

With lengthening of the carbon chain between the amino-groups and the thiourea residue naturally the formation of the unstable intermediate ring (II) is hindered and the degree of rearrangement is decreased[201,207].

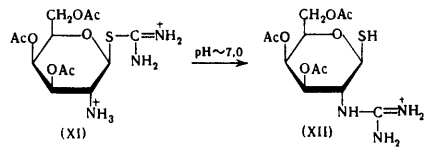
The difficulty of forming a seven-membered intermediate cyclic compound explains why the salt of *S*-4-aminobutylthiourea (VIII) is stable in aqueous solution at pH 7. However, on standing for several days at pH 9.2, a mixture of 4-mercaptobutylamine (IX) and 4-mercaptobutylguanidine (X) is formed, which, as has been shown[201] is the consequence of aminolysis:



(VIII) (IX) (X)

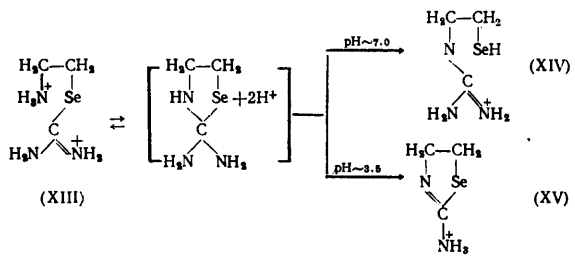
The introduction of alkyl substituents to the nitrogen atoms of amino-groups of the thiourea residue has no effect on the rearrangement of *S*-aminoalkylisothiouronium salts[201,208–210]. However, the presence of alkyl substituents at the nitrogen atoms of the amido-groups decreases the degree of "transguanidation". *S*-aminoalkyl-substituted thioureas, which contain one substituent at the nitrogen atom of the amido-group undergo rearrangement more easily than those which contain two substituents[208–210].

"Transguanidation" is also observed in a series of isothiuronium derivatives of hydrocarbons. Thus Wolfrom and coworkers[211,212] showed that at pH ≃ 7 the salt 2-(3,4,6-tri-*O*-acetyl-2-amino-2-desoxy-2-D-galactopyranosyl)-2-isothiourea (XI) is converted into the corresponding guanidinothiol (XII) by the scheme:



(XI) (XII)

In recent years information has also been published[208–210,213] about the analogous rearrangement of derivatives of isoselenourea. At pH ~ 7.0, 2-aminoethylisoselenourea (XIII) is converted into 2-guanidoethylselenol (XIV) but at pH ~ 3.5 2-aminoselenazoline (XV) is formed, that is, the reaction of "transguanidation" takes place by the usual scheme:



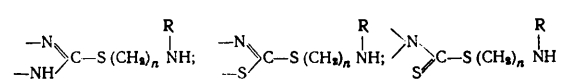
(XIII) (XIV) (XV)

The "transguanidation" rules, found by the examples of aminoalkyl-substituted isothioureas[201,207], extend also to the corresponding derivatives of isoselenourea[208–210]. The relative rate of rearrangement of the isothiuronium compounds and their selenium analogues were studied spectrophotometrically. It was found[208–210] that 2- and 3-aminoalkyl derivatives of isoselenourea undergo rearrangement much more rapidly than the corresponding thio-analogues. It was also observed[208–210] that aminoalkyl substituted isoselenoureas which contain a tertiary amino-group are, unlike the corresponding S analogues, capable of undergoing partial hydrolysis in a neutral medium, which is evidently explained by the C–Se bond being weaker than the C–S bond.

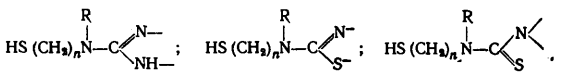
We assume that "transguanidation" can be considered as an instance of S → N (or Se → N) migration of an amidine group which takes place by the same mechanism as the migration of acyl groups in acylated amino-thiols.

VIII. REARRANGEMENT OF CERTAIN AMINOALKYL SULPHIDES

Naturally it was suggested that *S*-aminoalkyl derivatives of compounds which contain elements structurally similar to thiourea:

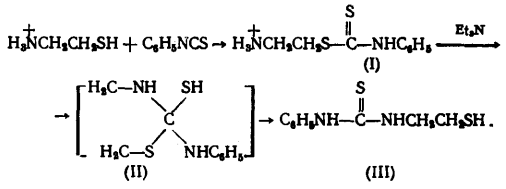


can also rearrange with formation of the corresponding *N*-substituted aminoalkane thiols:



Such rearrangements, which take place by the mechanism of S → N migration of acyl groups in the series of acylated amino-thiols, were also observed in *S*-aminoalkyl-substituted dithiocarbamates[214,215], xanthic[216] and trithiocarbonic[217] acids.

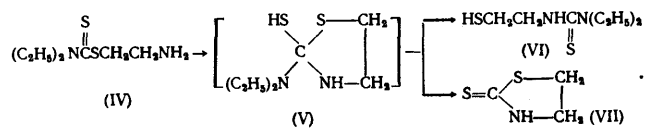
Thus, in the treatment of salts *S*-(2-aminoethyl)-*N*-phenyldithiocarbamate (I), obtained by the reaction of salts of 2-mercaptoethylamine with phenyl isothiocyanate, 1-(2-mercaptoethyl)-3-phenyl-2-thiourea (III) was liberated by one equivalent of a weak base[214]:



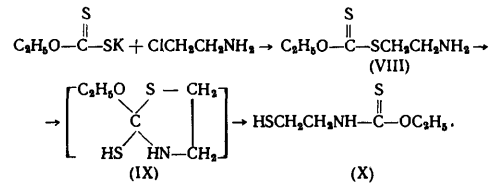
This rearrangement is a particular example of an S → N migration of a thiocarbamyl group and is also associated with the formation of an unstable thiazolidine ring (II).

Pustoshkin and Rachinskii[215] found that *S*-aminoethyl derivatives of diethyl dithiocarbamate undergo an analogous rearrangement in an alkaline medium. The reaction of sodium diethyldithiocarbamate with 2-chloroethylamine was first studied by Postovskii[218], who showed that the main product of the reaction is *S*-2-aminoethyldiethyldithiocarbamate (IV). Somewhat later Johnstone and Gallagher[219] noted, in repeating this work, that besides the compound (IV) another unidentified reaction product is also formed in large amount. This led Pustoshkin and Rachinskii to investigate the reaction in greater detail. As a result it was found that in an alkaline medium not only *S*-2-aminoethyldiethyldithiocarbamate (IV) is formed, but also a product of S → N rearrangement (VI) which does not exhibit salt-forming properties, is titrated by iodine, is readily oxidised by atmospheric oxygen and gives isothiuronium compounds with halogenoalkylamines.

It is natural to assume that here an intramolecular rearrangement of (IV) proceeds through the stage of formation of an unstable intermediate ring (V), which, depending on the conditions, is stabilised either in the form of an *NN'*-substituted thiourea (VI) by breaking of a C–S bond or as a 2-thiazolidinethione (VII) by loss of an amine molecule:



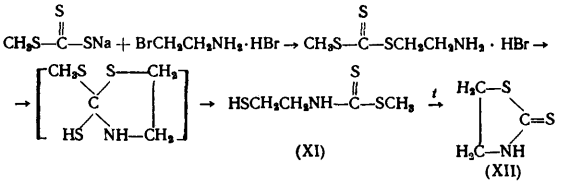
A rearrangement connected with S → N migration was also observed in a series of *S*-β(γ)-aminoalkyl derivatives of the ethyl xanthate[216]. The reaction of potassium xanthate with β-chloroethylamine in alcoholic solution at room temperature gave the ethyl *N*-2-mercaptoethyl monothiocarbamate (X), which is formed as a result of the rearrangement of *S*-2-aminoethylxanthate (VIII):



It has been shown[216] that the "transguanidation" rules are also retained here: the formation of the derivatives of ethyl monothiocarbamate was observed only when potassium xanthate reacts with halogenoalkylamines with a primary or secondary amino-group. Only the *S*-aminoalkyl xanthate is obtained for halogenoalkylamines with a tertiary amino-group or with a long carbon chain, when the formation of intermediate ring (IX) is hindered.

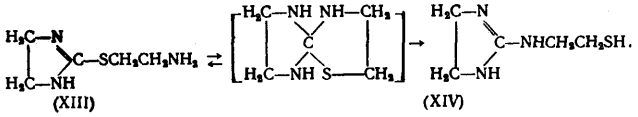
Here also the rearrangement can be regarded as S → N migration of a thioethoxycarbonyl group, taking place by the same mechanism as in derivatives of thioglycol[174].

An analogous S → N rearrangement was also observed in *S*-β(γ)-aminoalkyl-substituted esters of trithiocarbonic acids[217]. The reaction of sodium methyl trithiocarbonate with 2-bromoethylamine at low temperature gives methyl *N*-(2-mercaptoethyl) dithiocarbamate (XI), which is converted into 2-thiazolidinethione (XII) on heating:



Papers have recently appeared on the possibility of an S → N rearrangement in a series of *S*-aminoalkyl derivatives of certain heterocycles.

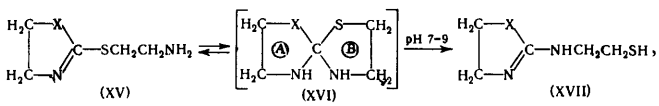
Khym and coworkers[201] showed that 2-(2-aminoethylmercapto)imidazoline (XIII) stable in 0.2 *N* HCl, at pH ~ 7.0, is converted into 2-(2-mercaptoethylamino)imidazoline (XIV) to the extent of 70% in 10 min, but the product of the rearrangement was not isolated and was only characterised chromatographically. In Khym's opinion the rearrangement proceeds thus:



Pavlova and coworkers[209,210,220] investigated the rearrangement of a considerable number of *S*-aminoalkyl derivatives of 2-mercaptoimidazoline containing primary, secondary, and tertiary amino-groups, over a wide range of pH. According to their results the conversion of these substances into *N*-substituted amino-thiols proceeds in accordance with the general mechanism of S → N rearrangement. They isolated the products of the rearrangement and characterised them as disulphides, whose structures were demonstrated by countersynthesis.

Subsequently an analogous rearrangement was studied by the example of the rearrangement of *S*-2(3)-aminoalkyl

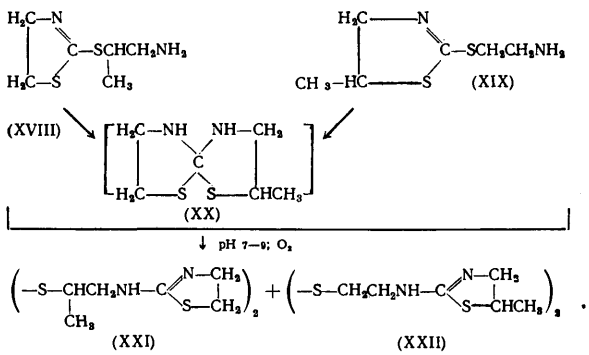
derivatives of 2-mercaptothiazoline [209,210,220,221] and 2-mercapto-oxazoline [222] into the corresponding thiols:



(XV) (XVI) (XVII)

where X = S, O.

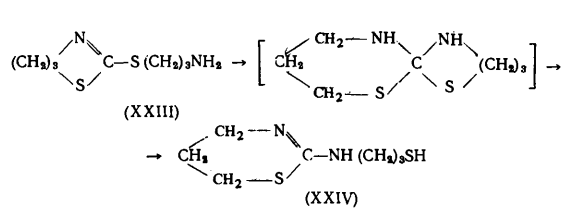
The assumption that the rearrangement of 2-(2-aminoethylmercapto)thiazoline (XV; X = S) proceeds with formation of an unstable intermediate bicyclic compound (XVI; X = S) naturally leads to the question as to which ring of the compound (XVI; X = S) is opened—that newly formed (B) or the original one (A)? To determine this, Pavlova and Rachinskii [210] obtained 2-(2-aminoisopropylmercapto)thiazoline (XVIII) and 2-(2-aminoethylmercapto)-5-methylthiazoline (XIX). It can be suggested that in the S → N rearrangement of these compounds the same intermediate bicyclic compound (XX) should be formed, in which the breaking of a C–S bond can proceed with the same probability in any ring of the compound (XX) and then the production of a mixture of the products (XXI) and (XXII) should be expected:



(XVIII) (XIX) (XX) (XXI) (XXII)

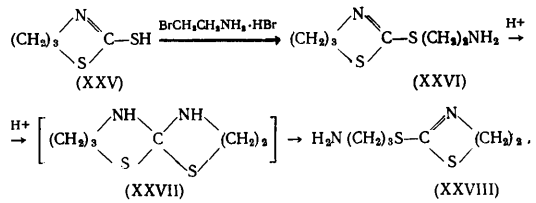
However, it was found [210] that the only product of the rearrangement of (XVIII) is 2-(2-thiazolinylamino)isopropylmercaptan, isolated as the disulphide (XXI) and for (XIX) bis-{β-[2-(5-methyl)thiazolinylamino]ethyl} disulphide (XXII). The results obtained suggest that the rearrangement of *S*-aminoalkyl derivatives of 2-mercaptothiazoline (and other heterocycles) does not proceed through the formation of the bicyclic intermediate spirane compound, but through a transition state.

Later Clapp and coworkers [223] studied the conversion of 2-(3-aminopropylthio)penthiazine (XXIII) into 2-(3-mercaptopropylamino)penthiazine (XXIV) in an alkaline medium:



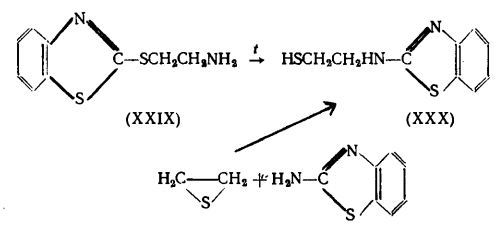
(XXIII) (XXIV)

At the same time, in the reaction of 2-thiopenthiazine (XXV) with 2-bromoethylammonium chloride instead of the expected 2-(2-aminoethylthio)penthiazine dihydrobromide (XXVI) the authors isolated 2-(3-aminopropylthio)thiazoline (XXVIII). It was suggested that the formation of (XXVIII) is the result of the rearrangement of (XXVI) in an acid medium through the intermediate compound (XXVII):



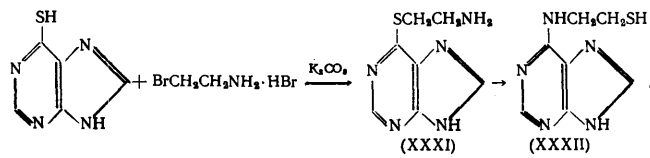
(XXV) (XXVI) (XXVII) (XXVIII)

In an attempt to bring about the rearrangement of *S*-2-aminoethyl derivatives of 2-mercaptobenzimidazole and 2-mercaptobenzthiazole it was found that these compounds do not form a thiol at pH 7–9 and room temperature [224]. Probably the difficulty of rearrangement is connected with a decrease in the positive charge on the $C_{(2)}$ carbon atom as a result of the influence of the double bond of the imidazole or thiazole ring. The results agree with the fact that in the reaction of 2-mercaptothiazole with halogenoalkylamines in an alkaline medium the corresponding *S*-aminoalkyl derivatives are obtained, and not the thiols, as the possible products of the rearrangement [225]. However, Manolov [226] succeeded in effecting the thermal rearrangement of 2-(2-aminoethylmercapto)benzthiazole (XXIX) into 2-(benzthiazol-2-ylamine)ethanethiol (XXX). The conversion of (XXIX) into (XXX) was carried out as follows: the base (XXIX) was heated in an atmosphere of nitrogen at 160°C for 1 h. The thiol (XXX) isolated as a result of the rearrangement of (XXIX) was shown chromatographically to be identical with the thiol obtained by the countersynthesis:



(XXIX) (XXX)

Johnston and Gallagher [227] observed the S → N rearrangement for derivatives of 6-mercaptopurine. In an attempt to obtain 6-(2-aminoethylthio)purine by the reaction of 6-mercaptopurine with 2-bromoethylammonium bromide in the presence of potassium carbonate, unchanged 6-mercaptopurine, β-purin-6-ylaminoethanthiol (XXXII), and the corresponding disulphide were isolated; the expected 6-(2-aminoethylthio)purine (XXXI) was not. As the authors proposed [227] (XXXI) is formed initially and in an alkaline medium it rearranged into β-purin-6-ylaminoethanethiol (XXXII):

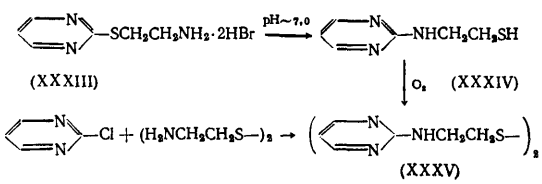


(XXXI) (XXXII)

Later a similar rearrangement was also described for *S*-aminoethyl derivatives of 8-mercapto- and 2-mercaptoadenine and also 8-mercaptocaffeine [228].

It was also found [210] that 2-(2-aminoethyl)mercaptopyrimidine (XXXIII) is rearranged into the corresponding *N*-substituted aminothiol (XXXIV) in neutral and slightly alkaline media. The product of the rearrangement, isolated

as a disulphide (XXXV), was identical with the product obtained by countersynthesis:



The rules for the S → N migration were studied in greater detail[209,210] by the example of the rearrangement of *S*-aminoalkyl-substituted 2-mercapto-4,6-diaminopyrimidine.

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We think that the results given above about the rearrangements associated with the intramolecular migration of acyl and other groups represent a generalisation of instances of the migration of groups sensitive to nucleophilic attack (structures which include the bonds C=O, C=S, or C=N) between two nucleophilic groups (H_2N, OH, SH). The study of the rules and limits of application of these rearrangements as well as being of general theoretical interest, opens a path to the synthesis of new organic compounds.

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Thermal Decomposition of Aliphatic Nitro-compounds

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Two mechanisms of decomposition of nitro-compounds are discussed: molecular, when a molecule of HNO_2 is detached and the corresponding alkene is formed, and free-radical, in which the reaction starts with the breaking of the C–N bond. Study of the reactions of the first type is of considerable interest in the light of the general theory of elimination reactions in the gas phase. The radical decomposition of nitroalkanes is characterised by high values of the pre-exponential factors. The activation energy in this instance equals the energy for breaking the bond. Secondary reactions have little influence on the rate of radical decomposition of *gem*-polynitroalkanes, therefore the study of the kinetics of the decomposition can be an effective method of determining the energy for the breaking of the C–N bond in these compounds. Bibliography of 48 references.

CONTENTS

I. Introduction 603
II. Decomposition of mononitro-compounds 604
1. Nitromethane 604
2. Nitroethane, 1-nitropropane, and 2-nitropropane 607
3. Chloropicrin 609
III. Polynitro-compounds 610
1. 2,2-Dinitropropane 610
2. Hexanitroethane 611

I. INTRODUCTION

The investigation of the kinetics of the reactions of thermal decomposition of aliphatic nitro-compounds began in the middle of the 1930s, when the first paper on the decomposition of nitromethane appeared[1], and several papers were published[2,3] which dealt with the thermal decomposition of chloropicrin. The mononitroalkanes nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane were the chief subjects of further investigations; these account for about three-quarters of all the work completed up till now. These four compounds were thoroughly studied by various authors in the period from 1950 to 1959, and the main features of their decomposition mechanisms were found. Considerably less attention has been paid to the polynitro-compounds. A quantitative study of the reactions during the decomposition of substances in this class was begun in 1962 and completed for only two compounds: 2,2-dinitropropane[4] and hexanitroethane[5]. Despite the comparatively small number of substances studied and the incompleteness of some of the studies, the results obtained are of considerable interest for the solution of a series of scientific and technical problems and merit careful examination.

The explanation of the mechanism of decomposition of nitro-compounds is inseparably connected with such problems as the determination of the energy of breaking of the C–N bond (and also bonds of another type) in substances of various structures, of finding the heats of formation of nitroalkyl free radicals, the conversion of free radicals in systems containing NO and NO_2, the influence of the state of aggregation and of the solvent on the radical reactions, topochemical processes in molecular crystals, and various other problems where the decomposition of nitro-compounds can serve as a model. A series of peculiarities of the reactions in the decomposition of nitro-compounds, for example, the possibility of decomposition by two competing mechanisms—radical and molecular—the dependence of these mechanisms on the structure of the molecule and the experimental conditions, and the existence of high pre-exponential factors in the radical decomposition are of undoubted interest to the theory of unimolecular reactions.

Among the technical problems which were responsible for the practical value of a study of the decomposition of nitro-compounds and to a certain extent stimulated these studies there is above all the industrial synthesis of mononitroalkanes by the vapour-phase nitration of hydrocarbons with nitrogen dioxide or nitric acid[6,7] and also the possibility of using certain nitroalkanes as additives to fuels for air-breathing and rocket engines[8].

The establishment of the detailed mechanism of the decomposition of any nitro-compound and the determination of the rate constants of the separate stages would have definite value in considering problems in the theory of combustion of liquid monopropellents.

A general introduction to the conditions and results of the studies of the reactions in the decomposition of nitro-compounds is given in Table 1.

In addition to Table 1, we note that the decomposition of all the substances except hexanitroethane was studied in the gas phase and in every instance the reaction obeyed a first-order law. Despite the simplicity of the formal kinetic laws there are often serious discrepancies between the results of different authors in determining the rate constants and for the choice of reliable quantities it is necessary to compare all the data. This is even more true of the treatment of the decomposition mechanism. A consideration of the accumulated material shows certain general features, inherent in the decomposition reactions of nitro-compounds, which in turn promote a better understanding of the mechanism of decomposition of other substances.

In connection with what has been stated above, in this review all the experimental data will be briefly examined, the mechanisms for the decomposition of nitro-compounds will be judged from various viewpoints, and the problems which we consider to be of greatest interest for further investigations will be emphasised.

Table 1. Some information about the reactions in the decomposition of the nitro-compounds.

Compound	Temp. range, °C	Decomposition conditions	E_{act}, kcal mole^{-1}	lg$A$ (A in s^{-1})	Hypothetical mechanism	Refs
1	2	3	4	5	6	7
Nitromethane	380–420	in a static system	61.0	–	CH_3–$NO_2 \rightarrow CH_3NO + O$	1
	310–440	ditto, P_0 = 4–40 mmHg	42.8	11.4	breaking of the C–N bond	9
	380–430	ditto, P_0 = 40–400 mmHg	53.6	14.6	ditto	10, 11
	420–480	in a flow system*, 6–18 mole % in N_2	50.0	13.4	$CH_3NO_2 \rightarrow CH_2O + HNO$	12, 13
	447	ditto, 0.04 mole % in He	–	–	breaking of the C–N bond	14
	355	in a static system, P_0 = 12.2–20 atm	–	–	$CH_3NO_2 \rightarrow CH_3NO + O$	15
	312–340	ditto, P_0 = 40 atm	49.2	13.73	breaking of a C–N bond	16
	430	in a flow system, in the presence of NO_2 and HNO_3	–	–	ditto	17
	872–1187	in a shock tube	13 ± 7	–	participation of excited states	18
	220–245	in a static system, P_0 = 36 atm over Cr_2O_3	36.0	11.0	breaking of a C–N bond or the formation of *aci*-forms	22
Nitroethane	310–440	ditto, 4–40 mmHg	41.5	11.53	breaking of C–N bond	9
	355–405	ditto, 50–405 mmHg	47.0	13.0	$C_2H_5NO_2 \rightarrow C_2H_4 + HNO_2$	19
	430–485	in a flow system, 0.04–0.5 mole % in He	39.0	11.0	breaking of C–N bond	14
	414–442	ditto, 10% in N_2	41.4	11.35	$C_2H_5NO_2 \rightarrow C_2H_4 + HNO_2$	20
	320–360	in a static system	39.7	10.83	ditto	21
	490–535	in a flow system, 10% in N_2	60.6	17.56	breaking of the C–N bond	21
	380–470	ditto, 10% in N_2	40.2	11.41	–	7
1-Nitropropane	210–440	in a static system, P_0 = 4–40 mmHg	41.5	11.73	breaking of C–N bond	9
	350–440	ditto	49.6	–	elimination of HNO_2	19
	430–477	in a flow system	48.5	13.30	breaking of C–N bond	14
	414–442	ditto	47.7	13.40	rearrangement $C_3H_7NO_2 \rightarrow C_2H_5CH{=}NOOH$	20
2-Nitropropane	310–440	in a static system, P_0 = 4–40 mmHg	39.0	11.34	breaking of C–N bond	9
	366–393	in a flow, 10% in N_2	39.0	11.00	elimination of HNO_2	20
	250–337	in a static system	39.3	11.05	ditto	23
Chloropicrin	138–170	ditto, 60–200 mmHg	37.67	15.69	rearrangement $CCl_3NO_2 \rightarrow Cl_2CO + ClNO$	2
	–	–	–	–	$CCl_3NO_2 \rightarrow CCl_2O + NO + Cl$	24
	–	–	–	–	breaking of C–N bond	25
2,2-Dinitropropane	175–210	ditto	50.5	18.5	breaking of C–N bond and chain process	4
Hexanitroethane	60–100	decomposition in the solid state	38.9	18.6	loss of two nitro-groups from one or two carbon atoms	5
	–	ditto**	39.0	17.4		
	60–100	solution in CCl_4	37.8	18.5		
	85–100	solution in n-heptane	28.0	13.0	formation of complexes with	
	85–100	solution in cyclohexane	21.0	9.1	solvent with transfer of charges	

* In all the experiments carried out by the flow method the total pressure was 1 atm.

** Personal communication of Rosen, cited in Ref.5.

II. DECOMPOSITION OF MONONITRO-COMPOUNDS

1. Nitromethane

Taylor and Vesselovsky, who first investigated the kinetics of thermal decomposition of nitromethane[1], found that under static conditions at initial vapour pressures of P_0 = 27–198 mmHg the reaction obeys a first-order equation and is homogeneous (the increase in the ratio of the surface to the volume of the reaction vessel by a factor of 6.3 has no influence on the initial rate of reaction). By distillation of the reaction products a small fraction with b.p. 84°C was isolated; this b.p. corresponds with that of formaldehyde oxime, an isomer of nitrosomethane. From this it was supposed that the first stage of the decomposition of nitromethane is the loss of oxygen from the nitro-group:

$$CH_3NO_2 \rightarrow CH_3NO + O\,. \qquad (1)$$

However, in an analysis of Taylor and Vesselovsky's experimental results Cottrell and coworkers noted[11] that the rate constant for the decomposition of nitromethane depends on the pressure, decreasing systematically with decrease in P_0. A more careful study of the decomposition of nitromethane, made by Cottrell and coworkers[10,11] by a manometric method, showed that the reaction is indeed homogeneous but the rate constant ceases to depend on the pressure only at an initial pressure $P_0 > 200$ mmHg.

In this connection criticism must be directed at both Taylor and Vesselovsky's results and those of Frejacquens[9], who determined the activation energy for the decomposition of nitromethane and the influence of other gases on the rate of this reaction at $P_0 = 4-40$ mmHg.

The activation energy found by Cottrell, 53.6 kcal mole^{-1}, was considerably less than that of Taylor (61 kcal mole^{-1}) and is in good agreement with the thermochemically determined energy for the dissociation of the C–N bond in CH_3NO_2†. This was an important point in support of a mechanism with primary breaking of the C–N bond. Cottrell's approximate thermochemical calculation[11] showed that $D(CH_3NO-O) \geqslant 73$ kcal mole^{-1}—that is, approximately the same value as $D(NO-O)$—and hence reaction (1) seems improbable.

A semiquantitative analysis of the decomposition products was made with the aid of various methods (infrared and mass spectroscopy, gas analysis). The main products were H_2O, CO, and CH_4 (Table 2). In addition small amounts of CO_2, N_2O, C_2H_4, and C_2H_6 were detected.

From these results, Cottrell proposed the following scheme for the decomposition of nitromethane[11]:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 , \quad (2)$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 , \quad (3)$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 , \quad (4)$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O , \quad (5)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 . \quad (6)$$

Table 2. Composition of the products (in mole fractions) in the initial stages of the decomposition of nitromethane at various pressures.

Product	200–400 mmHg (Ref.11) (420°C)	153 mmHg (Ref.15) (418°C)	12.2 atm (Ref.15) (355°C)	16.8 atm (Ref.15) (355°C)
CO_2	0.04	0.07	0.08	0.20
CO	0.31	0.51	0.17	0.21
CH_4	0.32	0.27	0.19	0.10
HCN	—	0.15	0.35	0.40
CH_3CN	—	traces	0.05	0.01
C_2H_5CN	—	—	0.04	0.01
CH_2O	—	—	0.06	0.04
NO	1.00	0.56	0.42	0.54
N_2O	0.03	0.02	0.02	0.04
N_2	—	0.10	0.04	0.01
H_2O	0.61	0.78	1.01	0.94
C_2H_6	0.01—0.02	0.02	—	—
C_2H_4	0.01	—	—	—

The possibility of the following reactions was also noted:

$$CH_2NO_2 \rightarrow CH_2O + NO , \quad (7)$$

$$CH_3 + NO \rightarrow CH_3NO \rightarrow HCN + H_2O . \quad (8)$$

After Cottrell's work, Hillenbrandt and Kilpatrik[12] studied the decomposition of nitromethane in a flow system.

Nitrogen saturated with water vapour was used as the carrier gas, and reproducible results were obtained by this procedure. The nitromethane was analysed polarographically. Formaldehyde (hydroxylamine method), methane, carbon monoxide, and nitrogen monoxide (adsorption gas analysis) were determined in the products. The rate of decomposition in the stream is independent of the changes in the nitromethane concentration for mole fractions between 0.06 and 0.18. The parameters of the Arrhenius equation are close to those obtained by Cottrell (Table 1). However, unlike Cottrell's results, a large proportion of formaldehyde was found in the decomposition products. The yield of formaldehyde per mole nitromethane was 0.5 mole in the initial stages at 420°C and reached 0.9 mole at 473°C. With increase in the extent of the conversion the yield of formaldehyde decreases, reaching a constant value of 0.4 mole at 473°C and 0.2 mole at 420°C. According to Cottrell's scheme, even allowing for reaction (7) the yield of formaldehyde cannot be $> 50\%$. Hillenbrandt and Kilpatrik suggested that the reaction proceeds at least partly by an intramolecular rearrangement:

$$CH_3NO_2 \rightarrow CH_2O + HNO . \quad (9)$$

The low concentration of formaldehyde in Cottrell's static experiments was explained by reaction (5), which proceeds very slowly at temperatures > 200°C.[29]

Hillenbrandt and Kilpatrik's conclusions were criticised by Gray and coworkers[14]. These authors investigated the kinetics of the decomposition of nitromethane, also under flow conditions (but at a lower concentration of nitromethane in the mixture), and determined the formaldehyde by reaction with dimedon; they found that the yield of formaldehyde is considerably less than had been claimed[12]. For example, at 447°C and a contact time of 1.1 s (extent of conversion 13%) the yield of formaldehyde was 16%. Gray considers that in the earlier work[12] there were two sources of error in determining the yield of formaldehyde: (1) the accuracy in calculating the $[CH_2O]/[CH_3NO_2]$ ratio decreases with decrease in the extent of decomposition; (2) it is possible that in the analysis the sum of the formaldehyde and formaldehyde oxime (obtained by isomerisation of nitrosomethane) was determined.

By use of metallic mirrors, Gray established that active free radicals are formed in the decomposition of nitromethane. He therefore supports Cottrell's viewpoint concerning the radical nature of the decomposition of nitromethane.

The formation of nitrosomethane (which under static conditions is converted into hydrogen cyanide and water) during the decomposition of nitromethane was proved convincingly by Müller, who studied the decomposition at 355°C in the range of pressures 12.2–20 atm. The reaction was studied by an ampoule method with mass spectrometric analysis of the nitromethane and the decomposition products. It was found that, in addition to nitric oxide and water, hydrogen cyanide is formed, its yield increasing with the pressure (Table 2). For comparison with Cottrell's results an experiment was run at 418°C and $P_0 = 158$ mmHg. Table 2, which gives these results, shows clearly that in addition to the products noted by Cottrell (CH_4, CO, NO, CO_2, H_2O) hydrogen cyanide and nitrogen are formed in comparatively large quantities.

To explain the large yield of hydrogen cyanide Müller suggested that the decomposition of nitromethane proceeds not solely by the Cottrell mechanism but partly by reaction (1) proposed by Taylor; the part played by this reaction increases with the pressure.

However, this conclusion was not convincing and has been criticised by Makovky and Gruenwald[16]. By using

† Three values for the heat of formation of nitromethane in the gas phase have been published: 17.8,[26] 12.35,[27] and 13.1[28] kcal mole^{-1}. The use of the last two values, obtained subsequently and evidently more accurate, gives for D(C–N) the values 52.0 and 52.7 kcal mole^{-1} respectively.

mass spectrometric analysis these authors found that the rate of decomposition of nitromethane at $P_0 > 1$ atm depends weakly on pressure, but the value of the activation energy determined at a pressure of 40 atm agrees well with Cottrell and Hillenbrandt's results (Table 1). The dependence on pressure of the hydrogen cyanide yield was confirmed and, furthermore, it was shown that its formation is facilitated by addition of nitric oxide to the nitromethane.

Makovky and Gruenwald consider that all these results are explained by Cottrell's scheme and the formation of hydrogen cyanide follows from reaction (8). The primary stage of this reaction—the formation of nitrosomethane—is termolecular and its rate depends more strongly on pressure than the rates of competing processes (3) and (10)‡:

$$CH_3 + NO_2 \rightarrow CH_3O + NO\ , \qquad (10)$$

which also explains the increase in the yield of hydrogen cyanide with increase in pressure.

From the material considered clearly Cottrell's scheme gives a satisfactory explanation for both the observed activation energy and the composition of the decomposition products. Therefore it can be considered correct in both features.

Additional information about secondary processes which take place during the decomposition of nitromethane can be obtained on considering the effect on the rate of this reaction of adding certain gases.

It was found[15,16] that the addition of NO_2 greatly retards the decomposition of nitromethane. Makovky explains this fact by the reversibility of reaction (2). As has been shown[30,31] in studies of the reactions of the methyl radical with nitrogen dioxide, this interaction takes place in two ways. The first leads to recombination:

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad (11)$$

and the second, to oxidation by Eqn. (10). Here $k_{10} \simeq 2k_{11}$.[30,32] In the decomposition of nitromethane the methyl radical not only reacts with nitrogen dioxide but also undergoes conversion by reaction (8) and possibly (3). A considerable yield of methane, especially at low pressures and in the initial stages, does not allow this reaction to be ruled out although with considerable concentrations of nitrogen dioxide and monoxide its role will be small. If it is assumed that the methyl radical is consumed only in reactions (3), (6), (10), and (11), then for the rate of decomposition of nitromethane under conditions when the concentration of methyl radical is stationary we obtain the expression§

$$-\frac{d[CH_3NO_2]}{dt} = k_3[CH_3NO_2]\left\{1 - \frac{k_{11}[NO_2] - k_3[CH_3NO_2]}{(k_{10}+k_{11})[NO_2] + k_7[NO] + k_3[CH_3NO_2]}\right\}. \qquad (12)$$

With a large excess of nitrogen dioxide the rate constant is $k_2[1 - k_{11}/(k_{10} + k_{11})]$ and if it is assumed that $k_{10} = 2k_{11}$ the rate can be expected to be ~ 30% less. As a matter of fact, the addition of 36–37% nitrogen dioxide reduces the rate of decomposition by approximately half[16]. This fact shows the presence of some other reactions of radicals with the nitromethane which are inhibited by additions of nitrogen dioxide. It should be noted that in studies of the decomposition of nitromethane the possibility of reaction (10) and the fate of the methoxy-radical have not been considered at all. This radical is undoubtedly formed in the decomposition of nitromethane and its recombination with nitrogen monoxide and dioxide hardly occurs at the temperatures of the experiments. Possibly the methoxy-radical is destroyed by the reactions:

$$CH_3O + NO \rightarrow CH_2O + HNO\ , \qquad (13)$$

$$CH_3O + NO_2 \rightarrow CH_2O + HNO_2\ , \qquad (14)$$

which also explains the absence of methanol in the decomposition products. Observations concerning the retarding action of nitrogen dioxide were made at temperatures not above 355°C, when it does not react directly with nitromethane. At higher temperatures the accelerating influence of nitrogen dioxide is observed. Thus Schay and coworkers[17] found, in studying the influence of nitrogen dioxide and nitric acid on the decomposition of nitromethane at 430°C with a contact time of 1–2 s, that both substances increase the rate of decomposition and at a concentration ratio of $NO_2 : CH_3NO_2 = 17 : 1$ the formation of polynitro-compounds is observed. These facts are explained by the reactions:

$$NO_2 + CH_3NO_2 \rightarrow HNO_2 + CH_2NO_2\ ,$$

$$NO_2 + CH_2NO_2 \rightarrow CH_2(NO_2)_2\ .$$

According to Eqn. (12) the addition of nitric oxide to nitromethane should accelerate the decomposition at $k_{11}[NO_2] > k_3[CH_3NO_2]$ and decrease the rate under the opposite conditions. Some observations[11,15,16] show that the addition of nitric oxide in amounts up to 10% to nitromethane does not alter the rate but at higher concentrations nitric oxide retards the decomposition. This fact can be taken as confirmation of the correctness of Cottrell's conclusion concerning reaction (3) in the scheme of decomposition of nitromethane.

Investigations by several authors[14–16] showed that the addition of oxygen accelerates the decomposition of nitromethane. For example, at 330°C and $P_0 = 40$ atm the addition of 8–35% oxygen increases the rate of decomposition by 20–25%.[15] The forward reaction of oxygen with nitromethane under these conditions is improbable, since oxygen is less active in reactions at the C–H bond than is nitrogen dioxide, for which the reaction with nitromethane is not observed. Possibly the oxygen affects the decomposition through the $CH_3OO^{\cdot}$ radical, which is formed in the reaction of oxygen with the methyl radical. The reaction of this radical with nitrogen monoxide and dioxide requires an activation energy. It is therefore comparatively long-lived and can react with nitromethane:

$$CH_3O\dot{O} + CH_3NO_2 \rightarrow CH_3OOH + CH_2NO_2\cdot . \qquad (15)$$

The decrease in the yield of hydrogen cyanide observed on adding oxygen[15] is indirect proof of the reaction of oxygen with methyl radicals.

The decomposition of nitromethane at high temperatures (872–1157°C) was studied by Bradley[18] with the aid of the shock tube method. The reaction was carried out in a mixture with argon (1 : 9) at pressures of 6–10 mmHg with analysis of the products every 50–100 μs on a time-of-flight mass spectrometer. The stoichiometry of the reaction corresponds to the equation:

$$2CH_3NO_2 \rightarrow CH_4 + CO + H_2O + 2NO\ .$$

The yields of methanol and formaldehyde are very small. The decrease in nitromethane equals the rate of formation of the products. Throughout the whole temperature range of the reaction the first-order equation is obeyed but the activation energy decreases as the temperature is raised, the mean value being 13 ± 7 kcal mole^{-1}.

‡Reaction (10) is not taken into account in Cottrell's scheme.

§ For k_7 read k_8 in Eqn. 12 (Ed. of Translation).

To explain these factors a mechanism was proposed which includes two successive excitations of the nitromethane molecules. However, before a definite conclusion can be drawn about the decomposition paths for nitromethane which are new in principle it is necessary to be convinced that the experiments were made in the range where the rate constants of the unimolecular reaction are independent of pressure.

The catalytic decomposition of nitromethane into various oxides was described by Makovky[32,33], who found that the decomposition is catalysed only by oxides which are basic. Evidently, the formation of *aci*-forms of nitromethane in layers adsorbed on oxides plays a part. The compounds can be arranged in the following order of catalytic activity:

$$Cr_2O_3>ThO_2>ZnO>MnO_2>CaO>Co_2O_3>TiO_2>PbO>MgO>$$
$$>CdO>HgO>Fe_2O_3>Al_2O_3>CuO>CeO_2>SbO_2>$$
$$V_2O_5, WO_3, CrO_3, MoO_3, SiO_2, P_2O_5$$

(the last does not act below 350°C). The decomposition of nitromethane over chromium oxide has been studied in most detail[22]. This catalyst has a very great effect on both the rate of decomposition (see Table 1) and the composition of the decomposition products, among which large proportions of ammonium hydrogen carbonate have been observed.

2. Nitroethane, 1-Nitropropane, and 2-Nitropropane

In distinction from nitromethane, the decomposition of which starts with rupture of the C–N bond, the decomposition of remaining mononitroalkanes that have been studied takes place (at least, at temperatures up to 450°C) by a unimolecular mechanism with elimination of nitric acid and formation of the corresponding alkene:

$$-\overset{H}{\underset{}{C}}-\overset{NO_2}{\underset{}{C}}- \rightarrow >C=C< + HNO_2. \qquad (16)$$

This mechanism was first proposed by Cottrell[19] in studying the decomposition of nitroethane and 1-nitropropane under static conditions. On using a manometric method, Cottrell found that the decomposition of nitroethane proceeds according to a first-order equation and is independent of the pressure at $P_0 > 30$ mmHg. The activation energy (~ 47 kcal mole^{-1}) was considerably below the dissociation energy of the C–N bond in this compound (56 kcal mole^{-1}) which can be evaluated from thermochemical data[26,28]. Infrared spectroscopy showed the presence in the products of CO_2 (~ 18%), NO (~ 45%), and C_2H_4 (~ 36%).

On the basis of these results Cottrell also proposed reaction (16), that is, a mechanism analogous to the molecular decomposition of alkyl halides[34]. This mechanism was disputed by Gray and coworkers[14]. The contradiction was resolved in the detailed studies by Wilde[20,21].

Gray investigated the kinetics of decomposition of nitroethane in flow at temperatures higher than in Cottrell's experiments. The mole fraction of nitroethane in helium was 4×10^{-4}–5×10^{-3}. Polarographic determination of the nitroethane was used to observe the reactions. CH_2O (by dimedon), NO_2 (Griess reaction), CO_2, NO, C_2H_4, C_2H_6 (adsorption analysis) were determined in the decomposition products. CO, CH_4, and N_2 were determined by the mass spectrometric method. The results of the analyses gave the following overall equation for the decomposition of nitromethane at 477°C:

$$C_2H_5NO_2 = 0.4\,C_2H_4 + 0.03\,C_2H_6 + 0.367\,CH_4 + 0.22\,CH_2O + 0.483\,CO + 0.07\,CO_2 + 0.657\,H_2O + 0.29\,N_2 + 0.08\,NO_2 + 0.34\,NO\,.$$

Gray found the activation energy to be 39 kcal mole^{-1}, even lower (and, as further investigation showed, more correct) than that of Cottrell. By the metallic mirror method Gray found that the decomposition of nitroethane at temperatures above 500°C is accompanied by the formation of free radicals. At the same time the artificial introduction of methyl radical (formed in the decomposition of di-t-butyl peroxide) depresses the decomposition temperature of nitroethane by a hundred degrees. One of the main products in this is formaldehyde. On the basis of these facts Gray proposed the following scheme for the decomposition of nitroethane:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2\,, \qquad (17)$$
$$C_2H_5 + NO_2 \rightarrow C_2H_5NO_2\,, \qquad (18)$$
$$C_2H_5 + NO_2 \rightarrow C_2H_5O + NO\,, \qquad (19)$$
$$C_2H_5O \rightarrow CH_2O + CH_3\,, \qquad (20)$$
$$C_2H_5O \rightarrow CH_3CHO + H\,, \qquad (21)$$
$$CH_3CHO \rightarrow CH_4 + CO\,, \qquad (22)$$
$$CH_3 + RH \rightarrow CH_4 + R\,, \qquad (23)$$
$$CH_3 + NO \rightarrow CH_3NOH \rightarrow HCN + H_2O\,. \qquad (8)$$

The formation of ethylene is explained by the reaction

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (24)$$

and partly by the occurrence of process (16). Furthermore, Gray assumes reaction of methyl radicals with nitroethane, which he thinks leads to the low value of the activation energy.

Wilde[20,21] carried out a detailed investigation of the decomposition of nitroethane in flow and under static conditions. In the first instance the method used was analogous to that employed by Hillenbrandt for nitromethane[12]. At a total pressure of 750 mmHg the rate of decomposition is independent of the composition of the $C_2H_5NO_2$–N_2 mixture. Nitroethane, acetaldehyde, and formaldehyde were determined polarographically, ethylene and nitrogen monoxide by chemical methods. It was shown that the main products (in the temperature range 414–442°C) are ethylene and nitric oxide. Hydrogen cyanide, water, and a little nitrogen dioxide were also observed, and at 442°C, methane and carbon monoxide. The discrepancy with Cottrell's results is explained by the fact that hydrogen cyanide, formaldehyde, and acetaldehyde are decomposed and oxidised under static conditions, giving, in particular, carbon dioxide. The activation energy determined for 412–442°C was 41.4 ± 1.1 kcal mole^{-1}. The inclusion of a point at 453°C gave the value 46.8 ± 3 kcal mole^{-1}, with much greater error.

Wilde also studied the decomposition of nitroethane under static conditions at lower temperatures (see Table 1), with analysis of the nitroethane by infrared spectroscopy. The temperature dependence of the rate constants obtained both under static and flow conditions (up to 442°C) are well described by a single Arrhenius' equation $k = 10^{10.83} \exp(-39\,700/RT)$ s^{-1}, with an activation energy almost equal to that determined by Gray. The same activation energy was found by Geiseler and Reinhardt[7] under flow conditions at 380–470°C.

Wilde considers that the high yield of ethylene combined with the low activation energy can be explained only within the framework of the Cottrell molecular mechanism, which (at least, up to 450°C) is the predominant path for the decomposition of nitroethane. Actually not one of the schemes including the primary decomposition of nitroethane at the C–N bond with subsequent formation of ethylene by the reaction:

$$C_2H_5 + NO_2 \rightarrow C_2H_4 + HNO_2 , \quad (25)$$

or

$$C_2H_5NO_2 \rightarrow C_2H_4NO_2 + HNO_2 , \quad (26)$$

$$C_2H_4NO_2 \rightarrow C_2H_4 + NO_2 , \quad (27)$$

can explain the low activation energy.

The low value of the pre-exponential factor ($\sim 10^{11}$ s^{-1}) also agrees well with this mechanism, as the most frequent reason for a low pre-exponential factors is[35,36] the formation of a cyclic transition state in which one or more internal rotational degrees of freedom are inhibited.

The existence of free radicals, observed by Gray at temperatures above 500°C and the formation of such products as CH_2O, CH_3CHO, HCN, CH_4, CO, and CO_2 cannot be explained without reference to free-radical processes. Wilde therefore suggests that part of the nitroethane decomposes by a radical mechanism (Gray's scheme), the fraction of which rises with the temperature. From Wilde's results, the decomposition at the C–N bond begins to affect significantly the total reaction rate for the decomposition at ~ 450°C. Consequently, at temperatures above 450°C a change in the mechanism of decomposition of nitroethane should occur.

To check this conclusion, Wilde investigated the decomposition of nitroethane at 400–525°C under flow conditions at contact times of 0.1–1 s.[21] Despite the high accuracy of the experiments it was found that the reaction obeys the first-order equation and the activation energy is 60.6 ± 5 kcal, that is, close to the energy of dissociation of the C–N bond in nitroethane. The same products were found qualitatively as were observed at low temperatures: ethylene, nitrogen monoxide, and formaldehyde.

Wilde considers that the high activation energy can be explained either within the framework of a non-chain radical decomposition:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 , \quad (17)$$

$$C_2H_5 + NO_2 \rightarrow C_2H_5O + NO. \quad (19)$$

$$C_2H_5O \rightarrow CH_3 + CH_2O , \quad (20)$$

$$CH_3 + NO \rightarrow HCN + H_2O , \quad (8)$$

$$C_2H_5 + NO_2 \rightarrow C_2H_4 + HNO_2 , \quad (25)$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2 , \quad (28)$$

or by a chain process:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 , \quad (17)$$

$$C_2H_5NO_2 + NO_2 \rightarrow C_2H_4NO_2 + HNO_2 , \quad (26)$$

$$C_2H_4NO_2 \rightarrow C_2H_4 + NO_2 , \quad (27)$$

for binary chain breaking (bimolecular decomposition of nitrogen dioxide or reaction of nitrogen dioxide with ethylene) should have an activation energy of ~ 50–55 kcal $mole^{-1}$.

A high value of the pre-exponential factor A found by experiment ($10^{17\pm1}$ s^{-1}) agrees best with a non-chain mechanism. Change of the molecular path of the decomposition to a radical one leading to a higher activation energy unavoidably suggests the existence of high values of A for stage (17). This conclusion can be easily correlated with theory[35–37] if it is assumed that in nitroethane rotation around the C–N bond is hindered. Many examples have shown that high pre-exponential factors in unimolecular reactions are observed when the initial state of the molecule has restricted internal rotational motion, which is freed in the formation of the transition complex. When a calculation was made (decomposition of C_2H_6 and N_2O_4) it was shown that replacement of the torsional vibrations by free internal rotation alone cannot give the experimentally observable increase in activation entropy and it is necessary to assume that a significant part is played by other types of motion (pronounced weakening of the deformation vibrations or even free three-dimensional rotation of the radicals in the activated molecule). Nitroethane is evidently not excluded from the general rule and the presence of a high pre-exponential factor in its decomposition is completely natural.

Similarly increased values of A can be expected for reactions of radical decomposition of any nitro-compounds having restricted rotation around the C–N bond.

The possible difference of 5–6 orders of magnitude between the pre-exponential factors of molecular and radical decompositions ensures successful competition for the latter at 400–450°C, even when the activation energy is 15–20 kcal $mole^{-1}$ greater than in molecular cleavage. In this connection a more careful study of the decomposition of nitroethane and other mononitro-compounds at high temperatures which would ensure the predominance of a radical mechanism, merits attention.

The decomposition of 1- and 2-nitropropanes at temperatures below 450°C proceeds as for nitroethane, according to a molecular mechanism[20]. The chief products are propene and nitrogen monoxide. The activation energy for the decomposition of 2-nitropropane is 39 kcal, and the pre-exponential factor has the diminished value of 10^{11} s^{-1}. 1-Nitropropane is characterised by a higher activation energy (Table 1) and the normal value of the pre-exponential factor. The last fact led Wilde to reject the mechanism of simple molecular elimination. Instead of it he advanced the hypothesis of the primary rearrangement of nitropropane with the formation of the *aci*-form:

$$CH_3CH_2CH_2NO_2 \rightarrow CH_3CH_2CH{=}NOOH ,$$

which is also the active species in the decomposition. Such explanation, in turn, seems improbable and hence the problem of the difference in the pre-exponential factor of 1-nitropropane from the corresponding values for the nitroethane and 2-nitropropane remains unsolved.

2-Nitropropane was studied in greater detail than 1-nitropropane. The rate of decomposition of this substance was determined by three methods—under static conditions using the yield of propene[23] and the change in total pressure[9], and also in flow from the decomposition of 2-nitropropane itself[20]. All three methods gave the same result (Table 1). Complete analysis of the decomposition products, carried out by Smith and Calvert[23] with the aid of mass spectrometry and gas chromatography, showed the considerable part played by side-processes in this reaction. At degrees of decomposition from 4 to 55% it was found that propene, nitric oxide, and water are formed in approximately equivalent amounts and constitute 65–75% of the total quantity of products. Acetone, acetonitrile, and formaldehyde amounted to 25–15% and various nitroalkane hydrocarbons, carbon monoxide and dioxide, to ~ 10%. The addition of propene did not affect and the addition of nitric oxide increases the rate of decomposition and alters the composition of the products (the

yield of nitroalkanes and acetonitrile is increased). The addition of nitrogen dioxide at 250°C did not affect the decomposition rate. Increasing the S/V ratio 100 times (by packing the vessel with glass wool) leads to a considerable increase in the rate and a rise in the yields of acetone, acetonitrile, and water. The ratio C_3H_6/NO is almost independent of the experimental conditions. The yield of propene does not alter on adding nitric oxide or propene itself nor on altering S/V. These facts show the formation of propene by the reaction:

$$(CH_3)_2CHNO_2 \rightarrow CH_3CH=CH_2 + HNO_2 .$$

As regards other carbonaceous products their production is explained by the occurrence of side-reactions, which occur because of the presence of the hydroxyl radical:

$$HNO_2 \rightarrow OH + NO \quad (29)$$

$$OH + CH_3CHNO_2CH_3 \rightarrow H_2O + CH_3\dot{C}NO_2CH_3 \quad (30)$$

$$OH + CH_3CHNO_2CH_3 \rightarrow H_2O + CH_3CHNO_2\dot{C}H_2 \quad (31)$$

$$CH_3\dot{C}NO_2CH_3 \rightarrow CH_3COCH_3 + NO \quad (32)$$

$$CH_3CHNO_2\dot{C}H_2 \rightarrow CH_3CHNO + CH_2O \quad (33)$$

$$CH_3CHNO_2\dot{C}H_2 \rightarrow CH_3CH=CH_2 + NO_2 \quad (34)$$

$$CH_3CHNO \rightarrow CH_3CNOH \quad (35)$$

$$CH_3CNOH + NO \rightarrow CH_3CN + HNO_2 . \quad (36)$$

The ratio CH_3CN/CH_3COCH_3 increases with the temperature, as reaction (31) has a higher activation energy than (30).

The weak link in the above scheme is reaction (29). The decomposition of nitric acid according to Eqn. (29) requires an activation energy of 48 kcal mole^{-1} and evidently cannot compete with reaction (28). Moreover, the assumption that the decomposition of nitrous acid initiates side-processes in the molecular decomposition of nitroalkanes cannot explain two features—the influence of the surface on the rate and the comparatively high yield of the products of radical origin at low temperatures—which distinguish 2-nitropropane from nitroethane and 1-nitropropane.

It is possible that in the decomposition of 2-nitropropane, because of its considerable acidity, a significant part is played by processes (decomposition of ionised form and reaction with nitric oxide) taking place in layers adsorbed on the surface.

In connection with the molecular mechanism of decomposition of mononitroalkanes a consideration of these reactions from the standpoint of the general theoretical concepts of gas phase eliminations merits attention. The most significant achievement in this region is the introduction of the concept of quasiheterolytic reactions in the gas phase[34,38]. It was shown[34] that in a series of gas-phase reactions just the same effect of substituents on the rate is observed as in ionic reactions of elimination or substitution, taking place in polar solvents. Hence the conclusion was drawn that the transition state of such gas-phase reactions has a polar nature and the internal supply of electrons is the main factor which determines the decomposition rate. In quantity and direction of the action of the substituents two types of quasiheterolytic reactions are distinguished. Reactions of the first type, which include the elimination of hydrogen halides from alkyl halides, are similar to S_N1 and $E1$ liquid-phase reactions; the reactions of the second type, represented by the elimination of alkenes from esters and alkyl vinyl ethers, are analogous to $E2$ reactions. Judging by the relative rates (Table 3) the decomposition of mononitroalkanes, at least in the quantitative respect, differs strongly from other eliminations in the gas phase. Nevertheless, from the standpoint of the polar nature of these reactions the nature of the change in activation energy in the series $C_2H_5NO_2$, n-$C_3H_7NO_2$, iso-$C_3H_7NO_2$ (39.7, 47.7, and 39.0 kcal mole^{-1} respectively) can be explained qualitatively. The value of the potential barrier for the detachment of HNO_2 from nitroalkanes $\epsilon_0 = E - Q$ (E is the activation energy, Q the heat of the process) varies symbathically with such properties as acidity or chemical shift of α-protons in the NMR spectra (Table 4), that is, it reflects the real change in the distribution of electron density in the molecule¶.

Table 3. Relative rates of reaction eliminations in the gas phase[34].

R	RCl	RBr	RNO_2^*	ROAc	HCO_2R	$ROCH{-}CH_2$
C_2H_5	1	1	1	1	1	1
n-C_3H_7	3.9	3.3	0.5	—	—	—
iso-C_3H_7	223	280	2.8	26	20	17

* The rates for the nitroalkanes were calculated from Wilde's results[20]. The temperatures of comparison were selected as for the alkyl halides[34].

Table 4. Correlation of the values of E and ϵ_0 with change in acidity and the chemical shift on the α-hydrogen atom.

Formula	E, kcal mole^{-1} (Ref.20)	Q^*, kcal mole^{-1}	ϵ_0, kcal mole^{-1}	pK	Chemical shift of α-H (in τ units) (Ref.42)
$C_2H_5NO_2$	41.4	16.1	25.3	8.49[39]	5.62
n-$C_3H_7NO_2$	47.7	14.6	33.1	8.98[40]	5.70
iso-$C_3H_7NO_2$	39.0	18.8	20.2	7.675[39]	5.42

* Data for the calculation taken from Refs.26 and 28.

The limited information does not allow more definite conclusions to be drawn about the nature of the molecular decomposition of mononitroalkanes, but undoubtedly these substances, being comparatively convenient for experimental investigation and exhibiting a great variety of structures, will merit attention as model compounds for studying gas-phase eliminations.

3. Chloropicrin

The first qualitative observation of the decomposition of chloropicrin CCl_3NO_2 was made in 1919 by Gardner and Fox[43]; on boiling (112°C), chloropicrin slowly decomposes into carbonyl chloride and nitrosyl chloride. In 1935 Rădulescu and Zamfirescu[3], using the method of titration of chloropicrin with permanganate, established the first order of the reaction for the decomposition and determined the rate constants at 130–160°C. Later[23] these results were used to estimate the activation energy, 40 kcal mole^{-1}.

¶ The reaction of nitrogen dioxide with an alkyl residue is evidently not limited solely to an induction mechanism. This is shown, for example, by the fine effects in the change in acidity of mono- and di-nitroalkanes[39-41]. It is easy to see that in the RX series, where X = Cl or Br (and the interaction of X with R is purely inductive), a linear relation is observed between ϵ_0 and Taft's induction constant σ^* of the group R.

In their detailed investigation of the decomposition of chloropicrin[23] Steacie and Smith found, with the aid of a manometric method, that the reaction proceeds homogeneously and is independent of P_0 in the range 60–200 mmHg. The decomposition products are carbonyl chloride, nitrosyl chloride, chlorine, and nitric oxide, the relative proportions of the last three compounds being close to equilibrium. Starting from these results a mechanism was proposed for the decomposition which included intramolecular rearrangement.

$$CCl_3NO_2 \rightarrow Cl_2CO + NOCl\,, \quad (37)$$

$$NOCl \rightleftarrows NO + {}^1/_2 Cl_2\,. \quad (38)$$

As, however, equilibrium (38) is established slowly (in the decomposition of chloropicrin to the extent of 50% there is 1% decomposition of the nitrosyl chloride at 160°C), to explain the observed composition of the products it was suggested that in stage (37) the activated molecule (NOCl*) is formed; this is rapidly decomposed into NO and Cl.

An analogous mechanism with primary decomposition of chloropicrin into carbonyl chloride, chlorine, and nitric oxide was proposed by Ashmore and Norrish[24].

In 1955, Gray[25] expressed the opinion that the decomposition of chloropicrin proceeds by a free radical mechanism and the first stage is the breaking of the C–N bond.

Gray's scheme:

$$CCl_3NO_2 \rightarrow CCl_3 + NO_2\,, \quad (39)$$

$$CCl_3 + NO_2 \rightarrow [CCl_3ONO] \rightarrow CCl_3O + NO\,, \quad (40)$$

$$CCl_3O \rightarrow Cl_2CO + Cl\,, \quad (41)$$

$$Cl + NO \rightleftarrows NOCl\,, \quad (42)$$

$$2Cl + M \rightarrow Cl_2 + M\,, \quad (43)$$

agree with all the experimental facts. The low value of the dissociation energy of the C–N bond, the value of which, according to the scheme, equals the activation energy of the decomposition can be attributed to the influence of three chlorine atoms[25]. In methane derivatives the introduction of electronegative substituents usually decreases the strength of the bonds[44]. This conclusion is indirectly confirmed by the force constant and frequency of the vibrations of the C–N bond in chloropicrin as compared with nitromethane (842 and 917 cm^{-1} respectively[45]).

The most convincing proof of the radical mechanism of the decomposition of chloropicrin gives an anomalously high value of its pre-exponential factor (Table 1). Only within the framework of the radical decomposition does this fact find a natural explanation (see p. 608). In rearrangements which include a cyclic transition state the pre-exponential factor can have only a normal or a low value.

Hence the replacement of hydrogen atoms in nitromethane by chlorine leads to a singificant decrease in the strength of the C–N bond and correspondingly to a very pronounced increase in the rate of decomposition. The mechanism of the first stage here remains unchanged but the secondary reactions in the case of chloropicrin are appreciably simpler and do not affect the initial state.

III. POLYNITRO-COMPOUNDS

Two of the polynitro-compounds (PNC) studied—2,2-dinitropropane (DNP)[4] and hexanitroethane (HNE)[5]—differ considerably in structure, decomposition rates, and the conditions under which their decomposition rates were studied. For these substances completely different mechanisms were proposed: breaking of the C–N bond and a chain process for DNP, and the formation of biradicals for HNE. Here, however, a situation analogous to that with chloropicrin is repeated. On closer examination it becomes almost certain that both substances have the same mechanism and decompose by a non-chain radical path with primary breaking of the C–N bond. Here the activation energy equals D(C–N).

1. 2,2-Dinitropropane

Fluornoy[4] studied the decomposition of DNP at 175–210°C by the ampoule method with mass spectroscopic analysis of the decomposition products. There are three initial products: acetone, nitric oxide, and nitrogen dioxide, which are formed in equivalent proportions. On increasing the extent of the decomposition the nitrogen dioxide concentration decreases rapidly (which is explained by its reaction with acetone) and carbon monoxide and dioxide and water appear. The rapid oxidation of acetone directly by nitrogen dioxide at temperatures above 100°C was shown in special experiments. At 2.3% decomposition the yield of nitrogen dioxide amounted to 75 mole % from the DNP and at 7.6% decomposition almost all the nitrogen of the products was found as nitric oxide. The decomposition of DNP proceeds homogeneously and the nature of the surface does not affect the reaction. The first-order rate constant is $3.2 \times 10^{18} \exp(-50\,500/RT)\ s^{-1}$.

Fluornoy considers that the decomposition of DNP starts with the breaking of the C–N bond, the strength of which should be less than in mononitro-compounds. The 2-nitropropyl radical formed in the first stage is converted into acetone, either on reaction with NO_2 with the intermediate formation of a nitro-nitrite:

$$(CH_3)_2\dot{C}NO_2 + NO_2 \rightarrow \left[O_2N{-}\overset{CH_3}{\underset{CH_3}{C}}{-}ONO \right] \rightarrow NO_2 + (CH_3)_2 + CO + NO \quad (44)$$

or intramolecularly according to (32), as Smith and Calvert assume (see p. 609). The direct unimolecular rearrangement of DNP into the nitro-nitrite is thought by Flournoy to be impossible owing to steric hindrance.

To explain the high pre-exponential factor, Flournoy suggested that in parallel with Eqn. (44) there is a reaction of the 2-nitropropyl radical directly with DNP:

$$(CH_3)_2\dot{C}NO_2 + (CH_3)_2C(NO_2)_2 \rightarrow (CH_3)_2C(NO_2)(ONO) + (CH_3)_2\dot{C}NO_2 \quad (45)$$

and hence the chain decomposition of the latter is effected. However, in the light of contemporary theory which allows the high value of A to be explained within the framework of a mechanism with breaking of a single bond (as occurs for nitromethane and chloropicrin) the hypothesis about chains is superfluous. Reaction (45) is evidently thermoneutral [$D(C{-}NO_2) \simeq D(C{-}ONO)$ [25]] and its activation energy should be not less than 10 kcal $mole^{-1}$. It is not known whether the 2-nitropropyl radical is removed by reaction with nitric oxide, but in the initial stages when there is a considerable concentration of nitrogen dioxide, reaction (45) cannot compete with (44) and the occurrence of the chain process is impossible.

We note that a high yield of acetone allows a molecular path for the decomposition of DNP to be excluded. Hence the change from mono- to *gem*-di-nitro-radicals is accompanied by a change in mechanism. The endothermicity of the reaction for loss of nitrous acid on going from 2-nitropropane to DNP can only decrease and even if it is assumed that the activation energy of the molecular decomposition is 15 kcal $mole^{-1}$ less than the strength of the

C–N bond (and the radical mechanism is affected only because of the high activation entropy), then $E \geqslant 35$ kcal mole^{-1} and the value of ϵ_0 (see p. 609) will be greater or equal to ϵ_0 for 2-nitropropane. The weakening of the C–N bond and the greater mobility of the β-hydrogen atom in *gem*-dinitro-compounds[46] should facilitate an increase in ϵ_0. As this does not take place, it can be assumed that the drop in electron density at the nitro-groups exerts an opposite effect and compensates the first two effects. A study of the decomposition of nitroalkanes of the type $RCH_2CH(NO_2)_2$ and $RCH_2C(NO_2)_3$ offers a further possibility of solving the problem of the competition of molecular and radical mechanisms.

2. Hexanitroethane

HNE is a strong oxidant and reacts with organic compounds of almost all classes[47]. Exceptions are hydrocarbons with branched chains and substances with a high concentration of halogens. A quantitative study of the decomposition was undertaken[5] for solid HNE and for dilute solutions (2×10^{-2}–4×10^{-2} M) in carbon tetrachloride, chloroform, perfluorokerosene, n-heptane, and cyclohexane. The reactions were observed by three methods: from the change in intensity of the absorption bands in the infrared spectra at 6.10 and 6.17 μm, from the yield of nitric oxide and dioxide, determined titrometrically, and manometrically from the increase in pressure of the decomposition products. All three methods give the same results. Tables 1 and 5 give the results on decomposition rates.

The agreement of the rates for decomposition in carbon tetrachloride, chloroform, and perfluorokerosene show the inertness of these solvents in relation to HNE. Hence the activation parameters found in carbon tetrachloride characterise the unimolecular decomposition of HNE. The decomposition in n-heptane and cyclohexane is considerably faster (and with a lower activation energy) than in inert solvents. This result is explained by the formation between HNE and the solvent of unstable molecular compounds of the charge-transfer complex type. Undoubtedly the aliphatic HNC exhibit electron acceptor properties, the strength of which increases with saturation of the molecule with nitro-groups. The idea of complex formation as a first stage in the interaction with different donors can play an important part in the study of the compatibility of PNC with other substances.

The decomposition of the HNE in the solid state proceeds more slowly than in inert solvents. The ratio of the constants k_{diss}/k_{solid} at 85°C is, according to Marshall and coworkers[5], 3.5; according to other results it is significantly greater, 56 (see Table 5). It should be noted that the accuracy of the determination of k_{solid} in this study[5] is somewhat doubtful. Thus the authors of this work write that the solid-state decomposition of HNE obeys a first-order equation. However, it is known that topochemical reactions never obey a first-order law and the reaction has to be accompanied by acceleration[48]. In this study[5] no information is given about the kinetics of the initial stage of the decomposition of HNE. Possibly acceleration of the reaction takes place in this stage and the value of k_{solid} corresponding to the initial rates will be less than that calculated[5]. Another reason for the differences in the available data can be the difference in the physical state and purity of the HNE specimens. The agreement of the activation energy in the decomposition of HNE in inert solvents and in the solid state suggests (by analogy with other instances[48] of the decomposition of solid organic substances) that the decomposition of HNE proceeds at places where there is pronounced strain in the ideal crystal lattice (surface micro-blocks, dissimilar type of defects) and the rate of reaction depends on the fraction of the molecules found at these points.

As noted by Marshall and coworkers[5], HNE itself is a fine model for investigating the regularity of the reactions of thermal decomposition of molecular crystals. The decomposition of HNE proceeds with an appreciable rate in the range of temperatures far from the melting point and is not accompanied by the formation of a liquid phase and condensed products, which could affect the reaction, by dissolving HNE or forming a new crystalline phase.

Table 5. Comparison of the rate constants (s^{-1}) for the decomposition of hexanitroethane in the solid state and in solutions.

t, °C	Solvent						
	without solvent	without solvent*	CCl_4	$CHCl_3$	perfluoro-kerosene	n-heptane	cyclo-hexane
85	$6.41 \cdot 10^{-6}$	$4 \cdot 10^{-7}$	$2.24 \cdot 10^{-5}$	$2.43 \cdot 10^{-5}$	—	$7.35 \cdot 10^{-5}$	$1.53 \cdot 10^{-4}$
100	$6.79 \cdot 10^{-5}$	$3.55 \cdot 10^{-6}$	$2.22 \cdot 10^{-4}$	—	$2.03 \cdot 10^{-4}$	$3.46 \cdot 10^{-4}$	$5.68 \cdot 10^{-4}$

* Private communication of Rosen cited in Ref.5.

The final products of the decomposition of HNE are nitrogen oxides and carbon oxides. Their composition corresponds approximately to the equation:

$$HNE \rightarrow 3NO_2 + NO + N_2O + 2CO_2,$$

and the rate of formation equals the rate of decomposition of HNE. The absence of information on the structure of the intermediate products does not permit any judgement about the secondary reactions, as a result of which the HNE molecule is destroyed. As possible primary stages of the decomposition two processes were proposed, including the simultaneous breaking of two nitro-groups

$$HNE \rightarrow (O_2N)_2\dot{C}-\dot{C}(NO_2)_2 + 2NO_2 \quad (46)$$

$$HNE \rightarrow (O_2N)_3C-\dot{C}(NO_2) + 2NO_2, \quad (47)$$

since the decomposition of the molecule into three species could explain the high values of the activation entropy. However, reactions (46) and (47) are no less than 10 kcal mole^{-1} more endothermic than the simple breaking of a single bond

$$HNE \rightarrow (O_2N)_3C\dot{C}(NO_2)_2 + NO_2 \quad (48)$$

and their occurrence is possible only for a considerably greater (by at least four orders of magnitude) pre-exponential factor. All this suggests that reaction (48) is the most probable primary act of decomposition of HNE. A conclusive solution of the problem is possible only on studying and comparing the decomposition of other PNC and determining the energy of the C–N bond in polynitro-derivatives of methane and ethane.

The problem of finding the energies of breaking of C–N bonds in aliphatic PNC has real prospects of solution in the study of thermal decompositions and makes it desirable to carry out further work to explain the mechanism of the decomposition of typical representatives of PNC of various structures. In experimental respects a study of these reactions should evidently not present great difficulty, since it can be expected that characteristic signs of the decomposition processes are general for DNP and HNE: the

combination of comparatively low activation energies with high pre-exponential factors, and in consequence the moderate decomposition temperatures at which nitrogen monoxide and dioxide found in the reaction products do not react with the initial components, do not inhibit chain processes, ensuring the unimolecularity of the process even under static conditions, the speed of the secondary reactions and the possibility of using a manometric method, is retained also for other nitro-compounds with a geminal distribution of the nitro-groups.

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Catalysis of Isotope Exchange in Molecular Oxygen and Its Application to the Study of Catalysts

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Problems related to the kinetics and mechanism of isotope exchange in molecular oxygen on solid catalysts are reviewed. Experimental data on the homomolecular exchange of oxygen on oxides and metals are reported. The relationship between the catalytic activity of oxides towards oxygen exchange and their activity towards other oxidation reactions is discussed. It is pointed out that studies of isotope exchange reactions of molecular oxygen should prove useful in elucidating the nature of intermediate entities during the interaction of oxygen with a catalyst surface. The activity towards exchange can be used as a characteristic of general oxygen reactivity, and rules for the choice of oxidation catalysts can be based on it.

CONTENTS

I. Introduction 613
II. Kinetics of isotope exchange in molecular oxygen 613
III. Experimental data on isotope exchange in molecular oxygen on solid catalysts 615
IV. Relationship between the catalytic activity of oxides towards oxygen exchange and their activity towards other oxidation reactions 623
V. Participation of oxygen from oxide catalysts in oxidation reactions 625

I. INTRODUCTION

The exchange of atoms between oxygen molecules (homomolecular isotope exchange)

$$^{16}O_2 + {}^{18}O_2 = 2{}^{16}O{}^{18}O \qquad (1)$$

is the simplest chemical reaction which oxygen can undergo. This provides a very convenient model reaction for investigating the rules which control the choice of catalysts, since it is not accompanied by changes in the chemical composition of the reaction mixture. The features of the homomolecular isotope exchange reactions provide information on the nature of the oxygen bond on the catalyst surface and can be useful in explaining the mechanism of catalytic oxidation reactions. The analogous isotope exchange reaction in molecular hydrogen has been the object of a large number of investigations, and has played an important role in elucidating the mechanism of catalytic hydrogenation reactions.

Studies of homomolecular exchange in oxygen began relatively recently. The first results for this reaction on magnesium and zinc oxides[1] were published by Winter as recently as 1954; this paper was followed by a paper relating to some other oxides[2]. The early results were reviewed by Winter[3], and compared with data on the rate of isotope exchange between molecular oxygen and the oxygen from the oxides, the rate of adsorption and the catalytic activity towards the oxidation of CO and the decomposition of N_2O. In later years, a great deal of work on homomolecular exchange in oxygen was published by Soviet scientists[4-32]. Foreign workers also are active in this field[33-37].

The present review attempts to generalise the results obtained so far and to consider the various possible relationships between the activity of catalysts towards homomolecular oxygen exchange and their activity towards other oxidation reactions, involving the transfer of oxygen atoms between reactant molecules.

II. KINETICS OF ISOTOPE EXCHANGE IN MOLECULAR OXYGEN

1. Method of Investigation

The course of reaction (1) is monitored mass-spectrometrically from the change in the intensity ratio of the peaks corresponding to masses 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$). Winter[3] worked with a static system, taking a continuous leak of a very small fraction of the reaction mixture to the mass spectrometer tube through a fine capillary. Some workers have sampled the gas for isotopic analysis at intervals, by means of ampoules removed from the apparatus and transferred to the mass spectrometer. To avoid the possibility of diffusion-controlled steps at high rates of exchange it is desirable to work with a circulating system[6].

Isotope exchange in molecular oxygen has been studied mainly on oxides[1-4,6-10,33,34], and less extensively on metals[4,5,11,20-22,35,36]. With oxides, exchange between molecular oxygen and oxygen from the oxide is possible as well as homomolecular exchange. In most of the work on the isotope exchange of molecular oxygen on oxides, conditions were such that the concentrations of ^{18}O in the solid (α_s) and in the gas (α) were equal. Some workers[9,19,28,34] studied exchange in molecular oxygen under conditions of simultaneous isotope exchange between the oxygen in the oxide and in the gas phase.

2. Kinetics of Isotope Exchange in Molecular Oxygen in the Absence of Isotope Exchange with the Catalyst

The kinetics of homomolecular oxygen exchange are described in this case ($\alpha_s = \alpha$) by a first-order equation. For

example, the change in the concentration of $^{16}O^{18}O$ molecules is

$$\frac{dC_{34}}{d\tau} = Z\frac{S}{N_g}(C_{34}^* - C_{34}) = k(C_{34}^* - C_{34}) \quad (2)$$

where Z is the total number of oxygen molecules, whatever their isotopic composition, which exchange atoms per unit time and unit catalyst surface, in molecules cm^{-2} s^{-1}; N_g is the total number of oxygen molecules in the gas phase; S is the surface area of the catalyst in cm^2; τ is time in s; C_{34}^* and C_{34} are the fractional numbers of $^{16}O^{18}O$ molecules at equilibrium and at time τ respectively. Integration of Eqn. (2) gives

$$k = \frac{1}{\tau}\ln\frac{C_{34}^* - C_{34}^0}{C_{34}^* - C_{34}} \quad (2a)$$

where C_{34}^0 is the fraction of $^{16}O^{18}O$ molecules at zero time.

Eqn. (2) is valid for any exchange mechanism[38]. The influence of the mechanism is manifest only in the dependence of the total number Z of exchanges upon the oxygen pressure P_{O_2} and the temperature T.

3. Kinetics of Exchange in Molecular Oxygen with Simultaneous Isotope Exchange with the Oxygen of the Catalyst

To elucidate the details of the exchange mechanism, it is often helpful to measure simultaneously the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the catalyst. In this case $\alpha \neq \alpha_s$, and the kinetics of the exchange become more complex.

Isotope exchange with the oxygen of the catalyst (for example, an oxide) includes dissociative adsorption with formation of adsorbed atoms or atomic ions, exchange of these adsorbed species with oxygen ions from the oxide, and desorption in the form of molecules[7].

The change in concentration of ^{18}O in the gas phase due to exchange with the oxygen of the catalyst is described by the equation

$$-\frac{d\alpha}{d\tau} = R\frac{S}{N_g}(\alpha - \alpha_s) = R'(\alpha - \alpha_s) \quad (3)$$

or, in the integral form,

$$R' = \frac{N_s}{N_g + N_s}\frac{1}{\tau}\ln\frac{\alpha^0 - \alpha^*}{\alpha - \alpha^*} \quad (3a)$$

Here R is the total number of exchanges between oxygen from the oxide and oxygen in the gas phase, in molecules cm^{-2} s^{-1}; N_s is the amount of accessible oxygen in the oxide (number of molecules); α^0, α^*, and α are the fractional amounts of ^{18}O at zero time, at equilibrium, and at time τ respectively.

The kinetics of exchange in molecular oxygen occurring simultaneously with isotope exchange with the oxygen of the catalyst have been considered in detail by Musykantov and coworkers[18]. Three kinetically different variants are possible.

1. Isotope exchange in molecular oxygen [reaction (1)] occurs without involving the oxygen of the catalyst. In this case $d\alpha/d\tau = 0$, and the change in concentration of $^{16}O^{18}O$ molecules is described by Eqn. (2).

2. Exchange in molecular oxygen involves one atom of oxygen from the catalyst. In this case

$$-\frac{d\alpha}{d\tau} = {}^1/_2 k_2(\alpha - \alpha_s) \quad (4)$$

and

$$\frac{dC_{34}}{d\tau} = k_2[\alpha(1-\alpha_s) + \alpha_s(1-\alpha) - C_{34}]. \quad (5)$$

3. Exchange in molecular oxygen involves two atoms of oxygen from the catalyst. In this case

$$-\frac{d\alpha}{d\tau} = k_3(\alpha - \alpha_s) \quad (6)$$

and

$$\frac{dC_{34}}{d\tau} = k_3[2\alpha_s(1-\alpha_s) - C_{34}]. \quad (7)$$

If the exchange occurs by all three mechanisms at the same time,

$$-\frac{d\alpha}{d\tau} = \left(\frac{k_2}{2} + k_3\right)(\alpha - \alpha_s) = R'(\alpha - \alpha_s) \quad (8)$$

$$\frac{dC_{34}}{d\tau} = k_1[2\alpha(1-\alpha) - C_{34}] + k_2[\alpha(1-\alpha_s) + \alpha_T(1-\alpha) - C_{34}] + k_3[2\alpha_s(1-\alpha_s) - C_{34}] \quad (9)$$

where $k_1 = Z_1S/N_g$, $k_2 = Z_2S/N_g$, $k_3 = Z_3S/N_g$, and Z_1, Z_2, Z_3 are the numbers of oxygen molecules (molecules cm^{-2} s^{-1}) which exchange atoms by the corresponding mechanisms.

Eqn. (9) can be recast[18] by inserting the value of α_s from Eqn. (8) and introducing the new variable

$$y = 2\alpha(1-\alpha) - C_{34} = C_{34}^* - C_{34}.$$

The physical significance of this variable is that of a driving force for the isotope exchange between oxygen molecules. In the absence of isotope exchange with the oxygen of the catalyst, the fractional change in the number of molecules would be proportional to y.

With this substitution, Eqn. (9) can be written in the form

$$\frac{dy}{d\tau} = -ky + \varphi\left(\frac{d\alpha}{d\tau}\right)^2 \quad (10)$$

where

$$\varphi = \frac{8k_3}{(k_2 + 2k_3)^2} \text{ and } k = k_1 + k_2 + k_3.$$

To solve the resulting system of differential equations we must know the variation of α_s with time of exchange. This variation can be quite complicated, because it is determined not only by the rate of exchange of surface oxygen atoms from the catalyst but also by the rate of diffusion of atoms which have been exchanged into the bulk of the catalyst. In its general form, the problem is soluble only in some special cases[18].

Generally speaking, the exchange constants k_1, k_2, k_3 can be evaluated by means of the differential equations (8) and (9) from experimentally found values of $d\alpha/d\tau$ and $dC_{34}/d\tau$ at different times. Reliable results can be obtained in this way only from a large number of measurements, which must be of the highest precision.

To characterise the role of the individual mechanisms, it is desirable to work with catalyst samples containing very small amounts of ^{18}O, whilst ensuring a high total concentration of this isotope in the molecular oxygen. Fig.1 shows the curves for the change in isotopic composition of the molecular oxygen, assuming different exchange mechanisms, for the case of $\alpha_s \ll \alpha$. If the concentration of the ^{18}O isotope in the enriched oxygen (from which the reaction mixture is prepared by dilution with ordinary oxygen) is in excess of 50%, we have $\alpha^0 > C_{34}^0$ at zero time. Hence it

is possible to identify the predominant exchange mechanism by the following qualitative rules:

a) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} = 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} > 0$, exchange occurs by mechanism *1*;

b) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} < 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} > 0$, mechanism *2* predominates;

c) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} < 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} < 0$, exchange occurs by mechanism *3*.

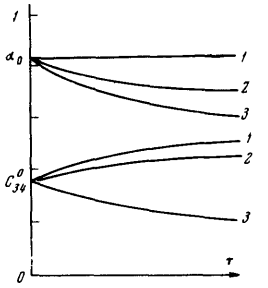

Figure 1. Change in isotopic composition of molecular oxygen for the different mechanisms of exchange. The numbers on the curves denote the exchange mechanism

Evidence for the third mechanism is provided also by a change in the ratio of the isotopic oxygen molecules (initially in homomolecular equilibrium) during exchange with oxygen from the oxide. If the exchange involves only the second mechanism ($k_3 = 0$), the homomolecular exchange equilibrium

$$\beta = \frac{C^2_{34}}{C_{32}\ C_{36}} = 4$$

will not be disturbed. Thus, if $k_3 = 0$, it follows that $\varphi = 0$, and from Eqn. (10) $dy/d\tau = 0$ under homomolecular equilibrium ($y = 0$).

Non-constancy of β during exchange is evidence that the exchange is occurring by the third mechanism.

All these conclusions involve the assumption of a uniform catalyst surface in respect of oxygen exchange. If the surface is not uniform, the constants k_1, k_2, and k_3 will vary from point to point on the surface. However, since exchange in this case will be confined to the most active regions of the surface, we can evaluate approximate exchange constants for these regions from experimental data for very small values of τ and $\alpha_s \ll \alpha$.

III. EXPERIMENTAL DATA ON ISOTOPE EXCHANGE IN MOLECULAR OXYGEN ON SOLID CATALYSTS

1. Catalytic Activity of Oxides

The influence of the conditions of pretreatment of oxides on their catalytic activity towards homomolecular oxygen exchange was first pointed out in Winter's review[3]. More recent work[14,16,24,29,31,33] has shown that in some cases the activity is greatly increased by a preliminary vacuum activation at high temperature, whereas oxygen treatment at high temperatures causes a sharp fall in activity. Some oxides showed differences in activity of several orders after different treatments. Since the change in activity caused by pretreatment under different conditions is evidently associated with a change in the oxygen content, it is desirable to compare the catalytic activity of the various oxides under two different headings: samples which have been treated in oxygen at a temperature high enough to ensure equilibrium composition of the surface layer, and samples having a non-equilibrium oxygen concentration in the surface layer.

2. Oxides with Equilibrium Oxygen Concentration in the Surface Layer

The main results (published since 1958) on the catalytic activity of oxides of equilibrium composition towards the isotope exchange reaction in molecular oxygen are summarised in Table 1. For comparison, the activity of platinum is also given in the Table.

Table 1. Kinetic characteristics of homomolecular exchange reactions of O_2 on various catalysts

Catalyst	Ranges of temp., °C	Ranges of oxygen pressure, mmHg	Surface area, $m^2\ g^{-1}$	Rate of exchange*, molecules $cm^{-2}\ s^{-1}$	Activation energy, kcal mole^{-1}	Pre-exponential factor, molecules $cm^{-2}\ s^{-1}$	Kinetic order with respect to oxygen	Literature references
Pt	200—250	0.15—0.5	0.4; 1.6	$6.7\cdot10^{13}$	16.5	$1.0\cdot10^{20}$	0.5	11
MgO	400—500	10	26	$1.8\cdot10^{7}$	40	$1.8\cdot10^{22}$	—	10
γ-Al_2O_3	400—500	10	190	$3\cdot10^{7}$	(32)	$3\cdot10^{19}$	—	10
TiO_2	530—600	40	67	$2\cdot10^{6}$	(39)	—	—	8
V_2O_5	450—550	5—240	2.7	$1\cdot10^{7}$	46	$1.9\cdot10^{24}$	0.7—0.8	6
Cr_2O_3	450—550	5—240	2.9	$6.1\cdot10^{7}$	42	$4.9\cdot10^{23}$	0.6—0.7	8
MnO_2	225—325	6—240	55	$2.1\cdot10^{13}$	22	$4.0\cdot10^{20}$	0.4	8
Fe_2O_3	350—450	6—240	27	$9.4\cdot10^{9}$	33	$2.7\cdot10^{23}$	0.6	8
Co_3O_4	125—250	4—240	7.7	$5.2\cdot10^{13}$	16	$5.2\cdot10^{19}$	0.4	8
NiO	225—300	5—120	7.7	$6.7\cdot10^{11}$	24	$6.7\cdot10^{20}$	0.4	8
CuO	250—350	4—240	18	$7.0\cdot10^{11}$	26	$3.9\cdot10^{21}$	0.4	8
ZnO	425—525	13—120	1.0	$3.7\cdot10^{8}$	40	$3.7\cdot10^{23}$	0.9	8
MoO_3	550—600	11—38	0.78	$2.6\cdot10^{8}$	69	$2.1\cdot10^{29}$	1.0	10
La_2O_3	400—450	20—40	28	$2.2\cdot10^{11}$	25	$7.0\cdot10^{19}$	1.1	28
CeO_2	320—420	14—80	29	$3.5\cdot10^{11}$	31	$1.2\cdot10^{23}$	1.0	28
Pr_6O_{11}	200—290	20—74	32	$4.4\cdot10^{13}$	20	$2.8\cdot10^{20}$	0.9	28
Nd_2O_3	200—300	6—80	26	$9.5\cdot10^{12}$	14	$5.6\cdot10^{17}$	1.1	28
Sm_2O_3	325—420	20—80	42	$1.1\cdot10^{13}$	14	$6.7\cdot10^{16}$	0.8	28
Gd_2O_3	300—370	20—80	31	$1.4\cdot10^{12}$	15	$1.8\cdot10^{17}$	1.1	28
Tb_4O_7	300—370	20—80	49	$2.8\cdot10^{12}$	24	$4.1\cdot10^{20}$	0.6	28
Dy_2O_3	326—420	20—84	49	$4.5\cdot10^{11}$	20	$2.9\cdot10^{17}$	0.9	28
Ho_2O_3	320—420	20—80	46	$3.8\cdot10^{11}$	25	$1.2\cdot10^{19}$	1.0	28
Er_2O_3	200—300	12—98	21	$3.1\cdot10^{13}$	18	$4.1\cdot10^{18}$	1.0	28
Tu_2O_3	300—420	20—80	22	$2.6\cdot10^{12}$	17	$1.5\cdot10^{18}$	1.0	28
Yb_2O_3	300—420	20—58	34	$2.6\cdot10^{11}$	20	$1.7\cdot10^{18}$	1.2	28
Lu_2O_3	300—420	20—80	20	$1.9\cdot10^{12}$	15	$2.5\cdot10^{17}$	1.1	28

* For MgO and γ-Al_2O_3 at 300°C and 10 mmHg, for the rare-earth oxides at 370°C and 20 mmHg, for the other catalysts at 300°C and 40 mmHg.

The oxides examined usually had a steady activity towards homomolecular exchange in oxygen, with the exception of NiO and CuO whose activity gradually fell to a stable value in 1–2 days[8]. Evidently, the conditions of treatment adopted had failed to ensure an equilibrium oxygen content in the surface layer of these oxides, and the achievement of phase equilibrium continued during the measurements of homomolecular oxygen exchange. The values listed in Table 1 refer to the stable activity of these oxides. The temperature dependence of the rate of exchange for a

series of oxides of the fourth period of the Periodic Table is shown in Fig. 2.

Some of the data listed in Table 1 differ from the results obtained by other workers. Thus, the rate of exchange observed by Winter[2] on NiO (from the carbonate) was approximately 100 times lower, and the activation energy was higher (35 kcal mole^{-1}). These discrepancies are probably due to different amounts of excess oxygen in the samples.

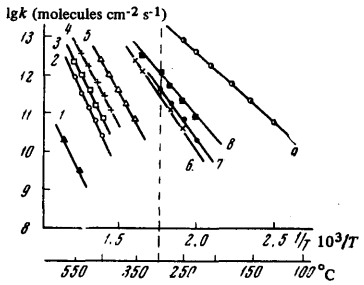

Figure 2. Temperature dependence of the rate of exchange of molecular oxygen on the oxides of metals from the fourth period: *1*) TiO_2; *2*) V_2O_5; *3*) Cr_2O_3; *4*) ZnO; *5*) Fe_2O_3; *6*) CuO; *7*) NiO; *8*) MnO_2; *9*) Co_3O_4.

The rate of exchange on Fe_2O_3 according to Winter[2] is close to the value given in Table 1, but the activation energy (19.2 kcal mole^{-1}) and the kinetic order with respect to oxygen (~ 1) are substantially different. According to Sazonov and coworkers[31], the activity of CeO_2 is approximately 40 times lower, and that of Gd_2O_3 4–8 times higher than Minachev and Antoshin's values[28], the activation energies being 31 and 10 kcal mole^{-1} respectively. These differences may be associated with the preparative conditions of the oxides. Sazonov and coworkers[27] studied the exchange in molecular oxygen on neodymium oxide, and found that the activity can vary by about an order of magnitude depending on the preparation and treatment conditions of the catalyst ($E = 30$ kcal mole^{-1}). The effect of the activation conditions on the catalytic activity towards homomolecular oxygen exchange, associated with a change in the oxygen content of the oxide, has been reported also for manganese dioxide[23].

Isotope exchange in molecular oxygen on oxides with an equilibrium oxygen concentration in the surface layer takes place in the temperature range where the surface oxygen has sufficient mobility and is able to exchange with the gas phase.

As regards their behaviour towards isotope exchange with the gas phase, the oxides investigated can be classified into the following groups.

1. Oxides in which the whole of the oxygen is equivalent. (The mobility of the oxygen in the lattice is greater than the rate of exchange with the gas phase.) This group includes V_2O_5,[39,40] CeO_2 [41] (oxygen diffusion in the CeO_2 lattice begins to affect the rate of exchange only above 440°C)[31], and MoO_3.

2. Oxides in which the surface oxygen has uniform mobility but exchange with the underlying layers of lattice oxygen is diffusion-limited. This group includes Fe_2O_3,[8,42] ZnO, Cr_2O_3,[8] Al_2O_3,[24] and the rare-earth oxides[41].

3. Oxides in which the surface oxygen is non-uniform towards isotope exchange with the gas phase. These are MnO_2,[42,43] Co_3O_4, NiO, and CuO.[8,42]

As an example, Fig. 3 shows the variation in the exchange rate as the fraction of exchangeable oxygen on the surface of MnO_2 is increased[23]. It is interesting to note that higher activation temperatures, which increase the activity of manganese dioxide towards oxygen isotope exchange, decrease the degree of non-uniformity of the surface oxygen. On raising the temperature of exchange the non-uniformity of the surface oxygen decreases.

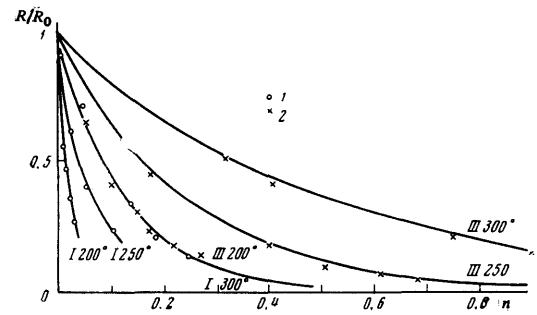

Figure 3. Decrease in the rate of exchange between O_2 and manganese dioxide with increase in the fraction of surface oxygen exchanged. The heat treatment temperatures were 350°C for preparation *I* (points *1*) and 550°C for preparation *III* (points *2*).

The NiO preparation investigated by Keier[44] showed uniformity of the surface oxygen, in contrast to the findings of other workers[8,42].

Winter[3] had noticed that on Cr_2O_3, NiO, and Fe_2O_3 the rates of exchange in molecular oxygen (Z) and of isotope exchange with the oxygen of the oxide (R) are closely similar. Subsequent work confirmed[8] that this behaviour is characteristic of all the oxides in which the equilibrium oxygen concentration is present. Results obtained[8] for transition metal oxides of the fourth period are listed in Table 2. The identity of the rates for the processes under discussion is particularly striking with the oxides in which the surface oxygen is uniform for isotope exchange with the gas phase (V_2O_5, Cr_2O_3, ZnO, Fe_2O_3). With these oxides the experimental values of the heteromolecular and homomolecular exchange rates agree within the limits of the inequality $R \leqslant Z \leqslant 2R$.

The rates of the exchange processes are more difficult to compare when the surface oxygen of the oxide is non-uniform and the rate of isotope exchange is lowered by confining the reaction to a monolayer. In this case the rate of exchange in molecular oxygen should coincide with the maximum initial rate of isotope exchange with the surface oxygen of the catalyst. Fig. 4 shows experimental results, obtained[23] on MnO_2, which support this argument. With Co_3O_4 a reliable determination of the initial rate of heteroexchange proved impossible.

Satisfactory agreement between the rates of hetero- and homo-molecular exchange was obtained also for the oxides CeO_2, Cd_2O_3, and Nd_2O_3.[27,31]

Several workers have examined the effect of various additives known to influence the semiconducting properties of the oxides on the rate of isotopic oxygen exchange.

Winter[2] studied oxygen exchange on NiO containing oxides of lithium, silver, and tungsten, and observed a rather weak correlation between the nature of the added oxide and the resulting change in rate. This may have been due to incomplete dissolution of the dopant at the low firing temperature used (650°C). According to Keier[44], the addition of 0.8 at. % of Li to NiO increased the exchange rate by a factor of 7–8 whilst the electrical conductivity rose by 5 orders of magnitude. The effect of the temperature at which the impurities are added to NiO was investigated by Gorgoraki and coworkers[29], who found that Li and In impurities added to NiO at 800°C had practically no effect on the activation energy: with the addition of lithium the reaction rate increases, but with the addition of indium it remains practically unaffected. Increasing the firing temperature of the preparation containing indium from 800° to 1200°C led to a sharp drop in reaction rate, possibly as a result of more complete dissolution of the impurity. Raising the firing temperature of pure NiO from 800° to 1200°C causes a slight drop in rate and an increase in the apparent activation energy of the exchange reaction.

Table 2. Comparison between rates of exchange in molecular oxygen and rates of isotope exchange with the oxygen of the oxide.

Oxide	Temp., °C	Rate of exchange, molecules $cm^{-2}\ s^{-1} \times 10^{-11}$	
		in molecular oxygen	with the oxygen of the oxide
V_2O_5	550	13.6	13.1
	550	2.4	1.7
Cr_2O_3	525	16.7	16.7
	400	0.31	0.63
ZnO	500	29.0	15.0
Fe_2O_3	400	6.8	4.7
NiO	300	6.8	6.8
CuO	300	5.7	4.7
MnO_2	300	21.0	25.0
	250	3.2	3.1

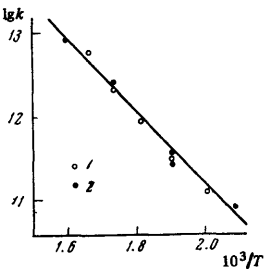

Figure 4. Comparison of the rates of exchange in molecular oxygen with the initial rates of exchange between O_2 and MnO_2: *1*) exchange in molecular oxygen; *2*) exchange with the oxygen of the oxide.

Gorgoraki and coworkers[12,13,45] studied the effect of Li, Ga, and In impurities on the activity of ZnO. Additions of lithium were found to increase the activity, whereas indium and gallium additions lowered it.

Margolis and Kiselev[5] studied the effect of adding the oxides Cr_2O_3, Bi_2O_3, and Li_2O to copper oxide.

Alkali metal sulphates are used as promoters in a variety of industrial vanadium catalysts[46]. Studies of the effect of alkali metal salts on the activity of V_2O_5 towards the isotope exchange of oxygen have shown that the mobility of oxygen in vanadium pentoxide is appreciably raised by alkali metal compounds[6,34,47-49]. As in the case of V_2O_5, volume diffusion of oxygen in the bulk of the promoted catalysts is much faster than the surface exchange. It is interesting to note that the promoted samples show very fast oxygen exchange not only of the vanadium pentoxide, but also of the impurity, whereas the oxygen of alkali metal salts does not in any way exchange with molecular oxygen under comparable conditions. The rates of hetero- and homo-molecular oxygen exchange on promoted vanadium pentoxide catalysts were found to be very similar[6].

Kasatkina and Antoshin[15] studied the isotope exchange between O_2 and CO_2 molecules and the heteroexchange of MnO_2 with O_2 and CO_2 on manganese dioxide which had been activated in a vacuum at 350°C. They found that the exchange of oxygen atoms between CO_2 molecules on the surface of manganese dioxide is much faster than reaction (1). The oxygen of MnO_2 proved to be very non-uniform towards exchange with CO_2: the first experimental points were obtained at extents of exchange of 8–16% of a monolayer, at which the rate of exchange is several times lower than the maximum. Later work from the same laboratory[23] showed that the rate of exchange of CO_2 with MnO_2, like the rate of exchange of O_2 within the limits of a monolayer, decreases exponentially as the extent of exchange increases. The initial rates of exchange of oxygen between CO_2 and MnO_2 calculated from the exponential law were identical to the rate of isotope exchange in molecular CO_2. The rate of isotope exchange between O_2 and CO_2 was much lower than the rate of isotope exchange between CO_2 and MnO_2, and was somewhat lower than (but of the same order as) the rate of exchange between O_2 and MnO_2. These results justify the conclusion that exchange between O_2 and CO_2 occurs through the exchange of these gases with the oxygen of the manganese dioxide surface, and that the exchange of molecular oxygen is the rate-limiting step.

Kiyoura[50] subsequently arrived at the same conclusions by studying the exchange between O_2 and CO_2 on the oxides TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, NiO, MnO_2, and Co_3O_4 at 150–600°C. On all these oxides the rate of exchange decreased in the sequence: CO_2–oxide > O_2–oxide > O_2–CO_2 (on the oxide).

Exchange between CO_2 and O_2 was observed only when exchange between molecular oxygen and the oxide was possible.

3. Basic Features of Exchange in Molecular Oxygen on Oxide Catalysts with Equilibrium Oxygen Content

a. Exchange mechanism. In view of the close similarity between the rates of homomolecular oxygen exchange and of isotopic exchange with the oxygen of the oxide, we may conclude that the simplest catalytic reaction—isotope exchange in molecular oxygen—occurs with participation of the oxygen from oxides with an equilibrium oxygen content. If the oxide has a uniform surface, the whole of the surface oxygen takes part in the reaction, but if the oxide surface is non-uniform, only the most active ("mobile") oxygen atoms are involved. Hence, of the possible exchange mechanisms discussed above, mechanism *1* is excluded for oxides with an equilibrium oxygen content. It is harder to establish whether isotope exchange in molecular oxygen occurs on these oxides by mechanism *2* or

by mechanism *3*, that is, whether one or two oxygen atoms from the catalyst are involved. The problem may be solved using an analysis of the exchange kinetics for the various mechanisms given above (p. 614).

Dzisyak and coworkers[8] have established qualitatively, from the time-changes of the quantity C_{34}/C_{36}, that exchange on V_2O_5 and on V_2O_5 doped with alkali metal sulphates occurs mainly with the participation of two oxygen atoms from the catalyst. Jiru and Novakova[34] independently reached the same conclusion for those catalysts.

Muzykantov and coworkers[19] quantitatively assessed the rates of exchange on V_2O_5 by different mechanisms by studying the exchange between V_2O_5 and oxygen of normal isotopic composition ($y_0 = 0$). They observed the change in the value of y with time of exchange (Fig. 5*a*), and found that y goes through a maximum when plotted against τ. By measuring $dy/d\tau$ at $\tau = 0$ and y_{max} from the experimental curves, the values of k_3 and k can be calculated[18]. Thus, substituting into Eqn. (10) the value of $d\alpha/d\tau$ from Eqn. (3), and assuming $y_0 = 0$, we obtain

$$k_3 = \frac{\left(\frac{dy}{d\tau}\right)_{\tau=0}}{2(\alpha^0 - \alpha^*)^2}\left(\frac{N_s}{N_g + N_s}\right)^2.$$

At the maximum, $dy/d\tau = 0$, and

$$k = \frac{\left(\frac{dy}{d\tau}\right)_{\tau=0}}{y_{max}\, e^{2r\tau}}, \text{where } r = \frac{N_g + N_s}{N_g N_s} SR.$$

Table 3. Homomolecular exchange of oxygen with simultaneous heteromolecular exchange between O_2 and V_2O_5.

Temperature, °C	p_{O_2}, mmHg	y_{max}, %	τ_{max}, min	R, molecules cm^{-2} s^{-1}	Z_3, molecules cm^{-2} s^{-1}	Z_3/Z
450	11	—	—	$4.6\cdot10^8$	$4.6\cdot10^8$	—
462	11	—	—	$1.1\cdot10^9$	$1.1\cdot10^9$	—
475	11	5.5	620±40	$1.9\cdot10^9$	$1.9\cdot10^9$	0.9—1.0
483	11	5.3	400±30	$2.5\cdot10^9$	$2.4\cdot10^9$	0.7—0.8
500	11	5.5	200±20	$5.1\cdot10^9$	$5.1\cdot10^9$	0.9—1.0
500	31	5.5	400±30	$7.8\cdot10^9$	$7.8\cdot10^9$	0.9—1.0
500	46	5.4	470±30	$9.6\cdot10^9$	$9.6\cdot10^9$	0.9—1.0

The results of this work are set out in Table 3. We can see that $Z_3 = R = Z$, i.e. $Z_2 = 0$ and $Z_1 = 0$, and therefore the exchange between molecular oxygen and the oxygen of vanadium pentoxide consists in the replacement of two atoms from the gas-phase molecule undergoing exchange by two atoms from the surface layer of the oxide. The observed rate of exchange is equal to the rate of the reversible surface dissociation of the oxide with formation of molecular oxygen.

Minachev and Antoshin[28] also observed, for all the oxides of the rare-earth elements except thulium and lutetium oxides, a departure from equilibrium in the gas phase during exchange with oxygen of equilibrium isotopic composition. Therefore, on these oxides also, exchange in molecular oxygen mainly involves two atoms of oxygen from the oxide in the elementary exchange act. The values of R, calculated for various oxides from the variation of α with τ, and of k_3, from data on the variation of y with τ during exchange on the same oxides (Fig. 5*b*), are very similar.

An unambiguous choice between mechanisms *2* and *3* cannot yet be made for the majority of oxides, due to lack of sufficiently accurate data. However, the similarity between the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the oxide is evidence that exchange on oxides of equilibrium oxygen content involves the participation of oxygen from the oxide, and therefore the rate of exchange should be a function of the energy and of the nature of the oxygen bond in the surface layer of the oxide.

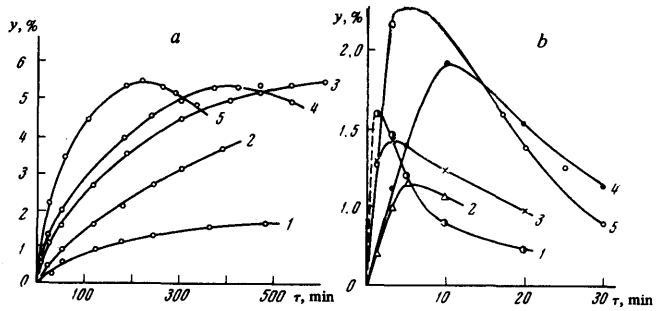

Figure 5. Variation of the quantity y with time of exchange; *a*) on V_2O_5 at 11 mmHg oxygen pressure, temperature (°C):
1) 450; *2*) 463; *3*) 475; *4*) 483; *5*) 500;
b) on rare-earth oxide at 370°C and 40 mmHg:
1) Nd_2O_3; *2*) Ho_2O_3; *3*) Dy_2O_3; *4*) CeO_2; *5*) CeO_2 (420°C).

b. Relationship between the catalytic activity towards exchange in molecular oxygen and other properties of the oxide. The oxygen bond energy in the surface layer of the oxide is uniquely determined by the electronic structure of the metal atom. Unfortunately, neither computational nor experimental methods of determining this energy are yet available. If, as a very rough approximation, the heat of formation per oxygen atom computed from thermodynamic data is used, the activation energy for the exchange reaction on oxides of metals from the fourth period is found to change monotonically with this quantity (see Fig. 6). The optimum bond energy corresponds to cobalt oxide, whereas in copper oxide the bond energy is apparently below the optimum.

On this basis, the study of oxides of metals from the fourth period can be divided into two groups. The oxides of the first group, including TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, and ZnO are characterised by a high bond energy, relatively low activity, and high activation energy for the exchange reaction. The kinetic order of the reaction with respect to oxygen is 0.6–0.8; the surface oxygen is uniform. All these oxides (except Cr_2O_3) are weakly semiconducting (*n*-type). The conductivity of chromic oxide is not yet clearly characterised: according to some measurements, this oxide exhibits *p*-type semiconductor properties after heat treatment in oxygen. For most of the oxides in this group, the number of electrons in the 3*d* shell of the cations corresponds to the most stable configuration: 0 for TiO_2 and V_2O_5, 5 for Fe_2O_3, and 10 for ZnO.

The second group comprises the oxides of lower oxygen bond energy: Co_3O_4, NiO, CuO, and MnO_2. On these oxides the exchange is fast, and is characterised by a low activation energy and a low pre-exponential factor. The order of the reaction is 0.3–0.4. The surface oxygen is not energetically uniform. The oxides of the second group,

on the whole, are *p*-type semiconductors of relatively high conductivity. The number of electrons in the 3*d* shell of the cations is 3 for MnO_2, 7 and 8 for Co_3O_4, 8 for NiO, and 9 for CuO.

The more active the oxide, the lower are the observed activation energy and pre-exponential factor. On going from the most active catalyst (Co_3O_4) to the relatively inactive V_2O_5, the activation energy increases by 30 kcal mole^{-1}, and the pre-exponential term increases by more than 4 orders of magnitude.

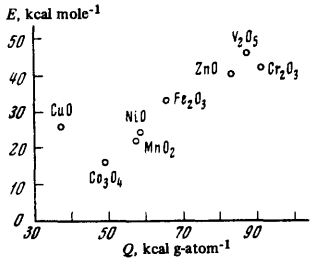

Figure 6. Correlation between the activation energy (E) for oxygen exchange on the oxides of fourth period metals and the heat of formation (Q) of the oxide referred to 1 g-atom of oxygen.

Winter noted breaks in the linear Arrhenius plots for the isotope exchange of oxygen with MgO [51] and ZnO [52], and for the homomolecular oxygen exchange on Cr_2O_3 [2] and on NiO from $Ni(NO_3)_2$.[3] These breaks correspond to a substantial decrease in activation energy at high temperatures. In our work[8], no such decrease in activation energy could be observed in the high-temperature region. Possibly, the drop in activation energy observed by Winter at high rates of exchange may have arisen from the onset of diffusional control, which was excluded in our work[8] by forced circulation of the reaction mixture.

Assuming that the rate-limiting step in the exchange is oxygen sorption (over the entire surface of the oxide), and that the active sorption complex is delocalised, the theory of absolute reaction rates[53] leads to the following value of the pre-exponential factor

$$k_0 = C_g \sqrt{\frac{kT}{2\pi m}}$$

where C_g is the concentration of sorbed molecules (cm^{-3}), k is Boltzmann's constant, and m is the mass of the molecule (grammes).

The maximum possible value of k_0 for the conditions corresponding to the data in Table 1 is 10^{22} molecules cm^{-2} s^{-1}. If the activated complex on the surface is localised, the theoretical value of the pre-exponential factor decreases. The loss of the translational degrees of freedom for motion along the surface and of the rotational degrees of freedom of the active complex lowers the theoretical value of k_0 by almost five orders of magnitude.

If desorption (again, over the entire surface) is rate-limiting, the maximum theoretical value of the pre-exponential factor rises to 10^{28} molecules cm^{-2} s^{-1}.

The experimental results listed in Table 1 show that the pre-exponential factor for the oxides of the first group is much greater than the maximum possible value for the rate of adsorption. Hence, we must conclude that the observed activation energy for the exchange is much higher than the activation energy for adsorption, and approaches the activation energy for desorption. Thus, for V_2O_5 the true activation energy for adsorption should be lower than the observed activation energy for exchange by at least 10 kcal mole^{-1}, in order to bring the value of k_0 below the theoretical maximum. This means that the surface of these oxides is effectively covered by oxygen, and oxygen removal is the rate-limiting step. This argument is supported by the fact that the rate of exchange on V_2O_5 was found to be approximately equal to the experimentally observed desorption rate.

In oxides of the second group the surface is, apparently, largely free to adsorb oxygen, and the observed activation energy for exchange is close to the true activation energy for sorption. The low value of the pre-exponential factor (as compared with the theoretical maximum) is probably the result of non-equivalence of the surface oxygen on these oxides. The degree of non-uniformity of the surface oxygen increases in the order $CuO < NiO < MnO_2 < Co_3O_4$. Hence it must be assumed that exchange in molecular oxygen occurs only on part of the surface of these oxides, the fraction of the surface involved being smaller, the greater the degree of non-uniformity. This explains the decrease in the pre-exponential factor on going from CuO to Co_3O_4. Low k_0 values may also arise from localisation of the active oxygen sorption complex.

These ideas on the relationship between the rate of exchange in molecular oxygen and the oxygen bond energy on the surface of the oxide can also be applied to the action of promoters in vanadium pentoxide. The addition of alkali metal sulphates to V_2O_5 leads to the formation of compounds close in composition to $V_2O_5.M_2SO_4$ and soluble in the excess of vanadium pentoxide. The oxygen bond energy in the resulting solid solutions is lowered, and therefore the activation energy decreases and the rate of exchange in molecular oxygen increases. The mobility of the oxygen increases, depending on the alkali metal, from lithium to caesium: in other words, the oxygen bond energy in a series of promoted catalysts changes monotonically with the atomic number of the alkali metal. As shown in Fig. 7, the rate and the activation energy of exchange on vanadium pentoxide promoted by alkali metal sulphates vary in the same sense as the electronegativity[54] of the alkali metal atom.

From Minachev and Antoshin's data[28], the change in the mobility of oxygen in the rare-earth oxide family is similar in character to the change in energy of the oxygen bond in the oxides. Inspection of Table 1 shows that the pre-exponential factor for these oxides is less than 10^{22} (with the exception of CeO_2). With CeO_2, the rate-limiting step in the exchange is apparently oxygen sorption over the entire surface of the oxide. The non-stoichiometric oxides of praseodymium and terbium, characterised by high concentrations of oxygen defects in the lattice, are the most active. Under exchange conditions all these oxides (except CeO_2) are *p*-type semiconductors.

c. Activity towards isotopic exchange of oxygen and semiconducting properties of oxides. During isotope exchange on oxides with equilibrium oxygen content, mutual transformations of molecular oxygen and atomic oxygen ions, involving electron transfer, must take place. Therefore, the electronic work function can be one of the terms which define the value of the activation energy for the exchange reaction. It is interesting

to establish whether a relationship exists between the catalytic activity towards isotope exchange in oxygen and the electronic work function. Experimental results[9] for a series of transition metal oxides are given in Table 4.

The activity was characterised by the rate of exchange at 300°C, and the work function by the contact potential difference between the oxide and gold[55]. The data of Table 4 suggest the lack of a simple correlation between catalytic activity and work function. For comparable values of the work function the catalytic activities of some oxides differ by five orders of magnitude, and for the same activity the work function can vary by more than 1 eV. It follows that the change in work function between different oxides is neither the only nor the main factor which determines the catalytic activity.

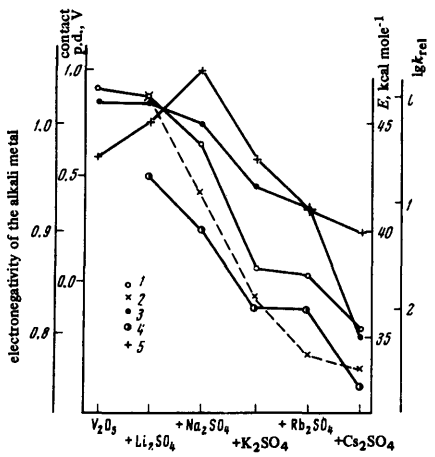

Figure 7. Activity of vanadium pentoxide promoted by alkali metal sulphates:
1) logarithm of the relative rate of exchange in molecular oxygen ($\lg k_{rel}$); *2*) logarithm of the relative rate of oxidation of SO_2 ($\lg k_{rel}$); *3*) activation energy of exchange (E); *4*) electronegativity of the alkali metal atom; *5*) electronic work function (contact p.d.).

Table 4. Catalytic activity and electronic work function of the oxides of metals of the fourth period.

Oxide	Contact potential difference against gold, V	Exchange rate at 300°C, molecules $cm^{-2}\ s^{-1} \times 10^{-10}$
TiO_2	−1.36	0.0002
V_2O_5	−0.75	0.001
Cr_2O_3	−0.10	0.0061
Fe_2O_3	−0.74	0.94
Co_3O_4	−0.13	5200
NiO	+1.02	68
CuO	−0.03	70
ZnO	0.0	0.037

In promoted oxides, also, the electronic work function bears no simple relationship to the catalytic activity towards oxygen exchange. Thus, the addition of 0.5 at. % of lithium or gallium to zinc oxide has the same effect on the work function (which is lowered in both cases), but the catalytic activity of zinc oxide is increased by a factor of 4 by the addition of lithium and is decreased by a factor of 5 by the addition of gallium[12].

Addition of alkali metal sulphates to vanadium pentoxide raises both the catalytic activity and the electrical conductivity[48]. Promotion with the sulphates of different alkali metals does not correlate with the change in electronic work function (see Fig. 7). Addition of 0.1 M potassium sulphate to vanadium pentoxide increases 50-fold the rate of isotope exchange in oxygen, but has no significant effect on the electronic work function.

4. Catalytic Activity of Oxides with Non-equilibrium Oxygen Content

Many workers[14,16,24,29-31,33] have found that the activity towards homomolecular oxygen exchange is very considerably increased by preliminary activation of the oxides in a vacuum. The effect was first noted on zinc oxide. Samples of zinc oxide which have been heated in oxygen before measurements of their catalytic activity show appreciable activity only at temperatures above 400°C. At 450°C, and 40 mmHg oxygen pressure, $Z = 4.8 \times 10^{11}$ molecules $cm^{-2}\ s^{-1}$.

Winter[1] studied the activity of ZnO after vacuum activation for 16 h at 630°C, the oxygen being admitted after the sample had been cooled to the temperature of the experiment. Under these conditions, exchange in molecular oxygen is detectable even at 120°C, and at 215°C the rate of exchange reached 8×10^9 molecules $cm^{-2}\ s^{-1}$. Barry and Stone[33] obtained even more striking results: one of their zinc oxide preparations had an activity of 8.1×10^{11} molecules $cm^{-2}\ s^{-1}$ at −193°C.

A detailed investigation of the low-temperature activity of zinc oxide[16] has shown that exchange on freshly activated preparations proceeds to equilibrium almost instantaneously at 25° and −194°C, but even after 2–2.5 min the rate of exchange drops to a measurable level (5.7×10^{13} at 25° and 4.34×10^{10} molecules $cm^{-2}\ s^{-1}$ at −194°C). After 5–8 h operation in oxygen at room temperature the rate of exchange becomes immeasurably low.

Exchange on copper oxide vacuum-activated at 400°C occurs with initial rates too high for accurate measurement between 0° and −78°C. Cuprous oxide heated in vacuum at 400°C is active towards isotope exchange in molecular oxygen over the wide temperature range between −196° and +200°C: at all temperatures the rate of exchange decreases with time, reaching a constant value after 20–60 min. The initial rate of exchange at 25°C is 1.5×10^{12} molecules $cm^{-2}\ s^{-1}$.

The rate of exchange on NiO [14,29] was 1.2×10^{13} molecules $cm^{-2}\ s^{-1}$ immediately after activation, decreasing by about a factor of 3 after 27 h.

Manganese dioxide[30] baked in vacuum at 350°C shows a stable activity over a fairly long period in the temperature range from −78° to +50°C. The rate of exchange at 25°C on MnO_2 is 2.1×10^{12} molecules $cm^{-2}\ s^{-1}$. The activation energy in this temperature region is 3.7 kcal $mole^{-1}$, the kinetic order with respect to oxygen is 0.64. From 50°C upwards the rate of exchange decreases appreciably with time, eventually reaching the value typical of manganese dioxide stored in oxygen. The decrease in exchange rate is faster at higher temperatures. The temperature dependence of the rate of exchange on MnO_2 is shown in Fig. 8*a*.

The deactivation of these oxides in oxygen at low temperatures is reversible: repeated vacuum activation at high temperatures fully restores the low-temperature activity. Exchange at high temperatures on ZnO produces an irreversible deactivation of the catalyst towards exchange at low temperatures[16]. The low-temperature ac-

tivity of MnO_2 is fully restored by vacuum activation irrespective of the deactivation temperature[30]. In the case of CuO, further activation after high-temperature exchange produces a decrease in the rate of exchange at low temperatures, i.e. the activity is not fully recovered.

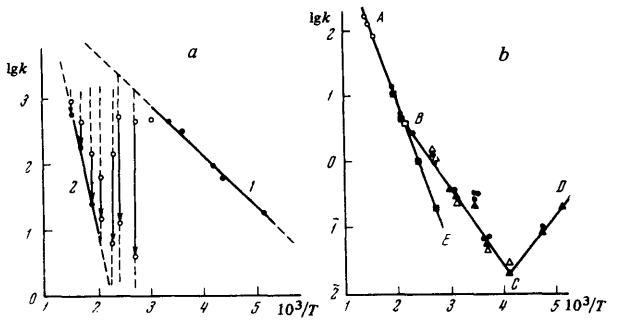

Figure 8. Temperature variation of the exchange rate in molecular oxygen; *a*) on MnO_2: *1*) with non-equilibrium oxygen content; *2*) with equilibrium oxygen content (open circles) and stable activity (filled circles), the unstable activity depending on the time of exposure of the catalyst to oxygen; *b*) on Gd_2O_3; *AE* high-temperature exchange on the oxide heated in oxygen, *BC* and *CD* low-temperature exchange on the oxide heated in a vacuum.

These results suggest the possibility of exchange by two different mechanisms, depending on the bond strength of the adsorbed oxygen to the oxide surface. Low-temperature exchange occurs only on catalysts which have been activated in a vacuum, i.e. under conditions when the oxide surface is strongly depleted of oxygen. This exchange does not involve participation of oxygen from the oxide: there is no isotopic exchange of oxygen between the oxide and the gas at low temperatures. Weakly adsorbed oxygen is probably involved. Exchange rates are high, and the activation energy low. Weakly adsorbed oxygen becomes more firmly bound, in time, to the surface of a vacuum-baked catalyst. This is accompanied by a decrease in the activity towards exchange by the low-temperature mechanism. The deactivation process is slow at low temperatures and fast at high temperatures. Therefore, the activity observed at high temperatures (even immediately after activation) corresponds to an oxide of surface composition close to—if not equal to—the equilibrium oxygen content. Under these conditions, isotope exchange between oxygen from the oxide and the gas takes place in parallel with homomolecular exchange. The rates of these processes are similar, and in this case the exchange in molecular oxygen proceeds through exchange with the oxide lattice. In the transition region of temperatures it is obviously possible, depending on the time of storage of the catalyst in oxygen, to observe homomolecular exchange at rates close to the rates characteristic of the low-temperature mechanism, or alternatively at rates close to those characteristic of the high-temperature mechanism.

The oxides of the rare-earth elements also show a low-temperature activity[31]. It is interesting to note that below 200°C the catalytic activity of gadolinium oxide heated in vacuum at 700°C for 4 h and rapidly cooled to room temperature remained stable even after prolonged storage (100 h) in oxygen at 20°C. The reproducibility of the measurements was adequate over the whole temperature range from −78° to +200°C and in both directions of temperature change. The low-temperature catalytic activity of the oxide began to change only after the catalyst had been heated in oxygen above 200°C, i.e. concurrently with the onset of isotope exchange between the gas phase and oxygen from the oxide. The temperature dependence of the activity of gadolinium oxide towards the isotope exchange of oxygen is illustrated in Fig. 8*b*. The presence of a break in the Arrhenius plot shows that the exchange can occur by different mechanisms, and the "negative" activation energy is evidence that the rate of exchange in the region *CD* is determined by the concentration of adsorbed oxygen, which increases with decrease of temperature.

Some interesting results have been obtained for γ-Al_2O_3.[17,24] The sample was prepared by thermal decomposition of the hydroxide followed by 10 h baking in air at 700°C. Exchange in molecular oxygen began at 350°C on a sample freshly prepared in this way. Vacuum treatment raised the activity of the catalyst, the effect increasing with temperature. Under these conditions, exchange was observed at temperatures as low as −78°C. The initial rates of exchange at 25°C and 10 mmHg oxygen pressure for various activation temperatures are tabulated below;

t, °C	300	350	400	450	500	600
Z_0, molecules $cm^{-2}\,s^{-1}$	0	$2\cdot10^{10}$	$3.5\cdot10^{10}$	$\sim10^{11}$	$5\cdot10^{11}$	$>10^{12}$

In an oxygen atmosphere the low-temperature activity of a vacuum baked sample decreases, rapidly at first and then slowly, reaching a stable value after 2–3 days: the rate is then 2–3 orders of magnitude less than the initial rate. Studies of the effects of temperature of heat treatment and of poisoning by water vapour on the activity of γ-Al_2O_3 lead to the conclusion that the active centres include sites remaining on the surface after removal of the OH groups[24].

Isotope exchange of molecular oxygen with oxygen from the oxide becomes appreciable in this case at a temperature of ~ 350°C, which is the same as the minimum activation temperature of γ-Al_2O_3 for low-temperature exchange in molecular oxygen, but the rate of hetero-exchange is approximately two orders of magnitude lower than the rate of homomolecular exchange. The whole of the oxygen on the surface of γ-Al_2O_3 takes part in hetero-exchange, whereas the active regions for homomolecular exchange occupy only a small fraction of the surface. These localised areas differ from the surface oxygen atoms which take part in exchange, as shown by the different response of the rates of hetero- and homo-molecular exchange to the conditions of pretreatment. Thus, increasing the degree of dehydration of γ-Al_2O_3 raises the rate of homomolecular exchange much more drastically than the rate of hetero-exchange, whereas oxygen treatment decreases the rate of homomolecular exchange but increases the rate of hetero-exchange[56].

Since there is no departure from homomolecular equilibrium following isotope exchange between molecular oxygen and the oxygen of γ-Al_2O_3 (i.e. $y = 0$), we conclude that hetero-exchange in this case involves the replacement of one atom from an adsorbed oxygen molecule by one oxygen atom from the surface layer of the oxide. A quantitative treatment of the experimental results for isotope exchange at 450°C indicates the following relative amounts of the various types of exchange: $k_1 = 0.95$, $k_2 = 0.05$, $k_3 = 0$.[24]

In every case, the high activity of the oxides at low temperatures arises from the formation of chemical defects at the oxide surface. In most cases these defects result from the loss of oxygen, and disappear after high-temperature treatment in oxygen. On γ-Al_2O_3 the active regions

can be of at least two types[56]: the first are formed by the loss of oxygen from the surface layer of the lattice during high-temperature treatment in a vacuum, and are poisoned by oxygen; the second are formed by the extensive dehydration of the surface during high-temperature treatment in a vacuum and in oxygen alike, and are stable to oxygen treatment but are rapidly poisoned by water vapour.

Isotope exchange of molecular oxygen on oxides which are active at low temperatures is not accompanied by isotope exchange with the oxygen of the oxide. This means that under these conditions the exchange does not involve the participation of oxygen from the oxide surface, i.e. the exchange proceeds exclusively by the first mechanism. It may take the form of dissociative adsorption and desorption, or the formation on the surface of a triatomic or tetratomic activated complex from one or two oxygen molecules. There are as yet no data on which to base a choice between these variants.

5. Catalytic Activity of Metals towards Molecular Oxygen Exchange

The isotope exchange of oxygen on metals was first investigated by Margolis[4]. Exchange was observed at 320°C on platinum after prolonged oxygen treatment at 300–400°C, and at 220°C on silver.

Margolis and Kiselev[5] examined the effect of chloride and iodide impurities in silver. On increasing the chloride concentration from 0.0015 to 0.015%, i.e. by a factor of 10, the rate of exchange fell by a factor of 3. Addition of iodine increased the rate of exchange of molecular oxygen.

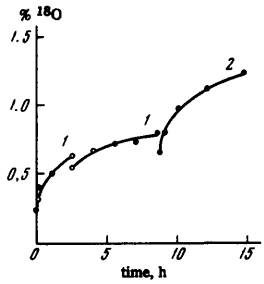

Figure 9. Isotopic exchange of molecular oxygen with oxygen adsorbed on platinum:
1) 200°C; *2*) 250°C.

Khasin and Boreskov[11] studied isotope exchange in oxygen on platinum films prepared by evaporation of platinum in a vacuum. The adsorption of oxygen on the freshly prepared films was measured at first, and found to include a fast stage and very slow stage. At 20°C the fast adsorption reached a coverage of 0.6×10^{15} atoms cm^{-2}, i.e. about half a monolayer, and at 250°C the amount of fast adsorption was in excess of a monolayer. Slow adsorption of oxygen took place throughout the experiment. The total amount of oxygen sorbed before starting the exchange experiments was 2–4 monolayers.

Even at 200°C the homomolecular exchange of oxygen on a platinum film occurs at a measurable rate. The activation energy of the exchange is 16.5 ± 1.5 kcal $mole^{-1}$. The kinetic order of the exchange reaction with respect to oxygen is close to 0.5.

The same films were used to study the exchange between adsorbed and molecular oxygen. Oxygen enriched with the heavy isotope (38% ^{18}O) was first adsorbed, the reaction vessel was filled with oxygen of normal isotopic composition, and the concentration of ^{18}O in the gas phase was monitored. The results are shown in Fig. 9. The discontinuities in the curve are due to the addition of natural oxygen to maintain the desired pressure, since the pressure is continually lowered by the removal of samples for analysis. The shape of the curves indicates a sharp decrease in exchange rate at low extents of exchange (below 0.1 of a monolayer), pointing to non-uniformity of the adsorbed oxygen.

The rate of exchange in molecular oxygen is the same as the maximum rate of exchange with adsorbed oxygen. The activation energy for exchange with adsorbed oxygen at an extent of exchange of 0.15 of a monolayer amounts to 28 ± 3 kcal $mole^{-1}$. Assuming appreciable non-uniformity of the adsorbed oxygen, the change in activation energy ΔE for the exchange with time τ can be calculated from the equation[57,58]

$$\Delta E = 2.3RT\,\Delta \lg \tau .$$

Fig. 10 shows the variation of the change in activation energy for exchange, measured in this way, with the extent of exchange x, defined as the fraction of a monolayer of adsorbed oxygen which has come to isotopic equilibrium with the gas phase. The dashed part of the curve is the extrapolation to $x = 0$. The results obtained justify the conclusion that oxygen adsorbed on a platinum film is non-uniform, and that the activation energy attending its exchange increases by 6 kcal $mole^{-1}$ over 25% of a monolayer. On the regions where homomolecular exchange takes place, the heat of adsorption of oxygen is ~ 13 kcal $mole^{-1}$, increasing to 28 kcal $mole^{-1}$ over 25% of a monolayer.

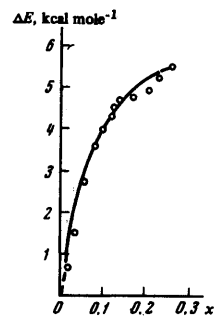

Figure 10. Change in the activation energy E for exchange of oxygen adsorbed on a platinum film with the extent of exchange x.

The exchange reaction in molecular oxygen occurs preferentially at zones which constitute ~ 3% of the total surface area of the platinum film. The higher rate of exchange of molecular oxygen found in this work (as compared with the results of Margolis[4]) is probably due to higher purity of the surface of the platinum film.

Subsequently[20–22], the homomolecular exchange of oxygen was studied on films of silver, palladium, and gold. It was shown that the rate of isotope exchange on palladium films is substantially decreased by oxidation of the metal,

pointing to a strengthening of the bond between adsorbed oxygen and the surface. Oxygen adsorbed on palladium films is energetically non-uniform. The bulk of this oxygen is barely mobile at 250°C, and is bound to the surface more firmly than in the case of silver. However, a very small fraction of the surface oxygen (< 2% of a monolayer) is very reactive towards exchange and plays a major role in the homomolecular isotope exchange reaction.

Oxygen adsorbed by a silver film at temperatures ≤ 200°C, and not exposed to higher temperatures, is uniformly accessible to exchange with gaseous oxygen at 200°C, suggesting that this oxygen is energetically uniform and has a high mobility. At 250°C part of this oxygen is transferred to a state which does not take part in exchange at 200°C: this state is characterised by a stronger bond to the silver.

Homomolecular exchange in oxygen on a gold film was negligible at 350° and 400°C.[22]

Comparative data for platinum, palladium, and silver are listed in Table 5. The difference in the interaction of oxygen with platinum and palladium surfaces on the one hand, and with silver surfaces on the other hand, evidently stems from the presence of *d*-orbitals in the first two metals, which can take part in bond formation with oxygen, whereas these orbitals are absent in silver[22].

Table 5. Comparison of the state of oxygen on films of platinum, palladium, and silver.

Metal	Rate of exchange at 250°C, Z^*, molecules $cm^{-2}\ s^{-1}$	Fraction of the surface involved in exchange, x	$\frac{Z}{x}$	Heat of adsorption of oxygen, kcal mole^{-1}	Activation energy of exchange, kcal mole^{-1}	Kinetic order with respect to oxygen
Pt	$7.83\cdot10^{12}$	~0.03	$\sim1.96\cdot10^{14}$	13	16±2	0.5
Pd	$4.22\cdot10^{11}$	<0.02	$>2.11\cdot10^{13}$	—	27—32	0.3
Ag	$2.41\cdot10^{12}$	~1	$\sim2.41\cdot10^{12}$	13	29—34	0.3

* Values of Z obtained at 0.5 mmHg oxygen pressure on Pt, 0.1 mmHg on Pd and Ag.

Sandler and Durigon[35] studied the homomolecular exchange and adsorption of oxygen on spongy silver, and found that at 160–180°C the chemisorption of oxygen is partially reversible, the rate of desorption being equal to the rate of exchange. They propose the existence of two forms of bond between chemisorbed oxygen and a silver surface. Increasing the amount of strongly bound oxygen lowers the rate of desorption, but does not affect the activation energy for desorption (32.5 kcal mole^{-1}). Fast diffusion and exchange occur over the whole of the surface, but only the oxygen less firmly bound to the surface is desorbed.

IV. RELATIONSHIP BETWEEN THE CATALYTIC ACTIVITY OF OXIDES TOWARDS OXYGEN EXCHANGE AND THEIR ACTIVITY TOWARDS OTHER OXIDATION REACTIONS

In the previous Sections we have shown that the catalytic activity of oxides and of oxygen-saturated metals towards the isotopic exchange of molecular oxygen is essentially determined by the energy of the bond between oxygen and the surface layer of the catalyst. It is natural to suppose that the oxygen bond energy may also be the key factor in other oxidation reactions taking place on these catalysts with the participation of oxygen.

It is interesting, therefore, to examine the catalytic activity of oxides towards these processes. The data chosen to be discussed here were confined to oxides with an equilibrium oxygen content. Accordingly, we select, for comparison, data on oxidation reactions taking place in an oxidising medium (i.e. with an excess of oxygen in the reaction mixture). It would have been very interesting to establish to what extent oxides with a non-equilibrium oxygen content, which show low-temperature activity towards oxygen exchange, can accelerate other oxidation reactions, but the available experimental material is insufficient for this purpose.

1. Catalytic Oxidation of Hydrogen

This reaction was studied by Popovskii and Boreskov[59] on the actual oxide samples used[8] to investigate isotopic exchange in molecular oxygen. The experiments were made by a stationary–circulation method[60], which allowed the reaction rate to be measured directly in the presence of a large excess of oxygen. The data for manganese dioxide are taken from the work of Bruns[61]. Complete consistency was found between the activity of transition metal oxides of the fourth period towards homomolecular oxygen exchange and towards the oxidation of hydrogen (curves *1* and *2* of Fig. 11). Consistency between changes in catalytic activity towards oxygen exchange and towards the oxidation of hydrogen is found also for vanadium catalysts promoted by alkali metal sulphates[48].

2. Oxidation of Carbon Monoxide

The very extensive literature on the activity of various oxides towards the oxidation of CO was reviewed by Krylov[62]. A statistical treatment was applied in an attempt to allow for the reliability of the various data by appropriate weighting factors. The relative activities of the oxides of the fourth period were found to be

MnO_2	Co_3O_4	NiO	CuO	ZnO	TiO_2	Fe_2O_3	V_2O_5	Cr_2O_3
310	200	100	83	22	18	16	11	11

This activity sequence with respect to the oxidation of CO is very close to the sequence found for the oxygen isotope exchange.

Stone[63] arrived at the following sequence of catalytic activities for the oxides by analysing published data on the oxidation of CO

$$CoO > NiO > MnO_2 \text{ from } 0° \text{ to } 150°C$$
$$CuO > Fe_2O_3 > ZnO > TiO_2 > Cr_2O_3 > V_2O_5 \text{ from } 150° \text{ to } 400°C$$

Again, the oxides of cobalt, nickel, manganese, and copper are the most active.

3. Complete Oxidation of Hydrocarbons

The results of a study of the activity of various catalysts towards the oxidation of methane in a flow–circulation apparatus are shown as curve *3* of Fig. 11. The change in specific catalytic activity for the series of fourth period oxides is similar to the change observed in the homomolecular exchange of oxygen. The same conclusion is reached if the comparison is made with the results of Gerald and

Horvatisch[65], who established the following activity sequence for the various catalysts

$$Co_3O_4 > MnO_2 > Pt > NiO > CuO > Cr_2O_3 > Fe_2O_3 > ZnO .$$

Stein and coworkers[66] made a systematic study of the activity of a large number of oxides towards the complete oxidation of hydrocarbons with five and six carbon atoms. The most active was Co_3O_4; a high activity was noted in most cases with manganese and nickel oxides; the lowest activity was shown by zinc oxide and vanadium pentoxide.

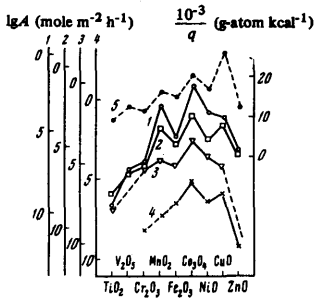

Figure 11. Specific catalytic activity of the oxides of metals from the fourth period towards oxidation reactions:
1) homomolecular oxygen isotope exchange; *2*) oxidation of hydrogen; *3*) oxidation of methane; *4*) decomposition of nitric oxide; *5*) reciprocal heats of formation of the oxides referred to 1 g-atom of oxygen.

Minachev and coworkers[67] studied the activity of the rare-earth oxides towards the complete oxidation of propene. They point out that the activity of these oxides appears in the temperature range corresponding to appreciable mobility of the surface oxygen[41]. A comparison of the extent of conversion of propene to CO_2 and of the rate of exchange of O_2 with the oxygen of the rare-earth oxides reveals a definite correspondence between these characteristics. The change in activity as a function of the atomic number of the element corresponds to the classification of these oxides into the cerium and the yttrium subgroups, both for oxygen exchange and for the oxidation of propene.

4. Oxidation of Ammonia

Kurin and Zakharov[68] found that the activity of the oxides of fourth period metals towards the high-pressure oxidation of ammonia decreases in the following order:

$$Co_3O_4 > MnO_2 > Cr_2O_3 > CuO > NiO > Fe_2O_3 > ZnO > TiO_2 .$$

Except for the position of chromium oxide, this series is very similar to the corresponding series for the isotope exchange reaction in oxygen.

5. Decomposition of Nitric Oxide

Curve *4* of Fig. 11 shows the relative catalytic activities of the oxides of the elements of the fourth period towards the decomposition of NO, measured in a static circulation apparatus[69]. MnO_2 and CuO were found to be unstable under the conditions of the reaction. The activity of the other oxides varies in the same sense as their activity towards homomolecular oxygen exchange.

6. Oxidation of Sulphur Dioxide

The activities of the various oxides towards this reaction cannot be compared, because most of them are converted into inactive sulphates under the conditions of the reaction. The only exception is vanadium pentoxide, whose activity is significantly increased by promotion with alkali metal sulphates.

As Fig. 7 shows, the catalytic activity of vanadium catalysts containing alkali metal sulphates varies in the same sense for isotope exchange in molecular oxygen and for the oxidation of sulphur dioxide.

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In spite of occasional discrepancies, not surprising in view of differences in sample preparation, purity, and experimental conditions, the examples considered undoubtedly show that the activity of oxides towards exchange in molecular oxygen is characteristic also of their activity towards various other oxidation reactions. In many cases, as for example in the oxidation of hydrogen, the correlation between the specific catalytic activities towards oxygen exchange and towards the oxidation reaction on the various catalysts is so striking that a common rate-limiting step for the two reactions can be postulated. For the hydrogen oxidation and the molecular oxygen exchange reactions this limiting step could be the chemisorption of oxygen. However, the activation energy and the kinetic order with respect to oxygen[9,59,70] of the oxygen exchange and the hydrogen oxidation reactions are quite different. Hence we must reject the hypothesis of a common rate-limiting step. The only possible conclusion is that although the rate-limiting steps of the two reactions are different, the catalytic activity depends on one and the same property of the oxides, which varies along the series of catalysts considered. It is natural to suppose that this property must be the bond energy between the oxygen and the surface layer of the oxide. In isotope exchange reactions this quantity determines the activation energy for adsorption and desorption of oxygen, and in the oxidation of hydrogen it determines the activation energy for the interaction of hydrogen with the oxygen on the oxide surface. In a similar way, the activation energy for the interaction of the reducing agent with the oxygen on the surface of the oxide can be determined as for other oxidation reactions by the binding energy of the oxygen on the surface layer of the oxide.

Thus, the binding energy of the oxygen is one of the basic factors controlling the activity of oxides towards oxidation reactions. However, the rate of isotope exchange in molecular oxygen, readily measured experimentally, can be a convenient quantitative criterion of the reactivity of the oxygen on the surface of an oxide.

Nevertheless, the prediction of the catalytic efficiency for oxidation reactions remains a complicated problem, since the simple dependence on the reactivity of the surface oxygen may be masked by the influence of numerous other factors. Thus, the catalytic activity may be limited by the stability of the oxide phase under the conditions of the catalytic reaction: an example of this behaviour is the oxidation of SO_2, discussed above, in which the activity of most oxides is extremely low because of their conversion into sulphates. If the Co_3O_4 phase had been more stable than cobalt sulphate under the conditions of the reactions,

cobalt catalysts would probably have been much more active than vanadium catalysts towards the oxidation of SO_2.

A complicated dependence on the reactivity of the surface oxygen can be expected also for partial oxidation reactions, in which the yield of the desired product is determined by the relative rates of a number of competitive and consecutive reactions.

In some cases the interaction between the material to be oxidised and the catalyst (chemisorption) can be the limiting step, instead of the subsequent reaction with the oxygen on the catalyst surface. The possibility that some oxidation reactions may proceed by interaction between the reducing agent and molecular oxygen cannot be excluded. This possibility has been examined in detail by Margolis[71]. In the latter two cases the correlation with the reactivity of the oxygen on the oxide surface may be very weak or altogether absent.

Lastly, even if the interaction with the oxygen on the oxide surface is the rate-limiting step, the simple correlation with the reactivity may be obscured by the decrease in the concentration of surface oxygen brought about by the reaction itself: this effect can have a profound influence on the properties of the surface oxygen. To a greater or lesser extent, this complication can be expected in all cases. It may be avoided, however, by measuring the reactivity of the oxygen on the oxide surface during the actual oxidation reaction.

In spite of the many complicating factors listed above, the bond energy of the oxygen in the surface layer of the oxide can be used as the basis for a generalisation of the experimental data and for the choice of catalysts for reactions involving the transfer of oxygen atoms between reactant molecules.

V. PARTICIPATION OF OXYGEN FROM OXIDE CATALYSTS IN OXIDATION REACTIONS

Transition metal oxides have found wide applications as the active components of oxidation catalysts. To explain the mechanism of oxidation reactions, involving the transfer of oxygen between molecules of the reacting materials, it is important to establish whether the oxygen of the catalyst plays a direct part in these transfers.

One possible assumption is that the oxygen to be added to the reducing component is taken from the surface layer of the crystal lattice of the catalyst, the oxygen loss in this layer being continuously replenished by the second component (capable of giving up oxygen). It must be stressed that these elementary processes of oxygen loss and oxygen addition involve no phase changes in the catalyst.

A second variant of the mechanism is based on the assumption that the transfer of oxygen from the oxidising to the reducing component takes place without intermediate conversion of the oxygen into an anion on the surface layer of the catalyst lattice. The energy and nature of the intermediate formed between the oxygen and the catalyst in this case are quite different from those of the oxygen bond in the oxide.

When comparing these variants, we should not try to reach a general conclusion. The correctness of one or other of the above assumptions depends on the nature of the catalyst, the nature of the reactants, and the conditions of the reaction. The discussion given in this review of the simplest oxidation reaction—isotope exchange in molecular oxygen—provides a good illustration of the state of affairs. With oxides which have been treated in oxygen at high temperatures, and whose surface layer therefore has acquired the equilibrium composition for the particular oxygen pressure, the rate of exchange in molecular oxygen is always the same as the rate of isotope exchange with the oxygen of the catalyst surface. This is evidence that the first of the above variants of the mechanism applies to this reaction. The form of the intermediate in the reaction between oxygen and the catalyst coincides, in this case, with the form of the oxygen bond in the surface layer of the oxide (or is so close to it that fast transitions between them are possible). The existence of other forms of atomically bound oxygen is unlikely under these conditions, and in any case the rate of formation of such structures should be considerably lower than the rate of binding of the oxygen in the surface layer of the oxide, since the exchange of molecular oxygen would otherwise take place through this form and its rate would be higher than the rate of exchange with oxygen.

On the other hand, oxides with a non-equilibrium oxygen content in the surface layer, prepared by a special heat treatment and active towards exchange at relatively low temperatures, give a rate of exchange in molecular oxygen considerably in excess of the rate of exchange with the oxygen of the oxide. This proves beyond doubt the correctness of the second variant of the mechanism.

These results can be of use also in identifying the mechanism of more complex oxidation reactions. The rate of exchange of molecular oxygen is characteristic of the rate of binding of oxygen by the catalyst. If the oxidation reaction takes place through the same intermediate form, produced by the interaction of oxygen with the catalyst, this step will be common to the two reactions. Simple comparison of the rates is not sufficient, however, to identify the mechanism of the oxidation reaction.

Because of the reaction with the component to be oxidised, the concentration of oxygen in the surface layer of the oxide under the conditions of the oxidation reaction may be lower—and the rate of binding of oxygen may therefore be significantly higher—than under conditions of exchange of molecular oxygen on oxides with an equilibrium oxygen content. Therefore, a rate of oxidation higher than the rate of exchange for the same temperature and oxygen pressure does not preclude oxidation through interaction with the oxygen of the oxide. Direct measurements of the rate of transfer of oxygen from the oxide to the reaction products are needed. These measurements are possible in principle (by introducing the heavy oxygen isotope into the oxide composition), but unambiguous conclusions are not always possible because of complicating factors.

Most of the work has been on the oxidation of carbon monoxide on manganese dioxide, copper oxide, and some other oxides. The first investigations[72,73] led to the conclusion that the oxygen of the oxide catalysts takes part in the reaction. On the other hand, Vainshtein and Turovskii[74,75] failed to observe a significant change in the isotopic composition of the catalyst after oxidising CO on MnO_2 and CuO enriched with ^{18}O. The sensitivity of the method would have allowed ~ 5% exchange of the oxygen of the catalyst to be detected, corresponding to several monolayers. The authors suggested, on the evidence of stepwise oxidation experiments on reduced oxides by successive additions of oxygen of different isotopic composition, that the mobility of oxygen in their oxides was high enough to ensure a uniform isotopic composition in the bulk and on the surface under the conditions of the experiment. However, direct measurements of the mobility of oxygen in MnO_2 [43] and CuO [42] have shown that the oxygen has no significant mobility in these oxides under the conditions of the CO oxidation experiments. Therefore, the work of Vainshtein and Turovskii, which showed that oxygen from the

bulk of the oxides does not take part in the oxidation of CO on MnO_2 and CuO, leaves unresolved the question of whether the oxygen on the surface of the catalyst (and, more to the point, the most active part of this oxygen) takes part in the reaction.

Winter[76] studied the mechanism of the oxidation of CO on NiO and Cr_2O_3 and concluded that only a small fraction (no more than 2.5%) of the surface oxygen of the catalyst was involved. With Cu_2O, however, between 10 and 40% of the surface oxygen took part in the reaction, the fraction increasing at higher reaction temperatures.

Popovskii and coworkers[77], in their work on the participation of oxygen from the surface of Co_3O_4 in the oxidation of hydrogen at 75°C, found that between 2 and 20% reacted if the sample had been activated at 400°C, whereas between 13 and 39% of the surface oxygen reacted on a sample which had been merely evacuated at 75°C. The low precision of these measurements is due to the need to apply corrections for the exchange of oxygen isotopes between the catalyst and the water vapour formed by the reaction.

Roiter and coworkers studied the participation in oxidation reactions of the oxygen of vanadium pentoxide with the help of ^{18}O. In the oxidation of naphthalene[78] on ^{18}O-enriched vanadium pentoxide the concentration of this isotope in the catalyst did not decrease within the limits of the measurement accuracy (~ 10%). If the whole of the oxygen used in the oxidation of naphthalene had been taken from the surface of the vanadium pentoxide, with complete mixing of the oxygen within the catalyst, the final concentration of ^{18}O in the vanadium pentoxide should have been 10–30% lower than the initial concentration. The authors concluded that the oxygen of vanadium pentoxide does not take part in the oxidation of naphthalene. This conclusion cannot be accepted unreservedly in view of the low mobility of oxygen within vanadium pentoxide crystals, inferred from the large departure from first order of the exchange kinetics in water vapour[40] at these temperatures (340–390°C).

In the oxidation of sulphur dioxide on ^{18}O-enriched vanadium pentoxide[79] the concentration of this isotope was found to decrease, but by no more than after oxygen exchange under the same conditions. If oxygen from the V_2O_5 surface had been involved in the oxidation of SO_2, the loss of ^{18}O from the catalyst should have been accelerated by the reaction. At the higher experimental temperatures of this work (500–610°C) inadequate mobility of the oxygen from the catalyst ceases to be an obstacle. The result of Kasatkina and Shustov[80] do not support these conclusions: these workers showed that SO_3 exchanges with the oxygen of vanadium pentoxide at a rate well in excess of the rate of oxidation of sulphur dioxide. This observation adds further complexity to the problem of the participation of oxygen from the oxide in the reaction.

Roiter and Yuza[70] made separate measurements of the rates of reduction of vanadium pentoxide by hydrogen and of oxidation by oxygen, and by comparing the results with the rate of the catalytic oxidation of hydrogen on V_2O_5 they concluded that the oxygen of vanadium pentoxide does not enter into the catalytic reaction.

All these researches enable us to conclude with some confidence that oxygen from the bulk of the oxides does not take part in catalytic oxidation reactions. This conclusion is in keeping with the general proposition that reactions involving a phase transformation cannot be invoked as stages of a catalytic process. The problem of whether oxygen from the surface of the oxides is involved in catalytic oxidation is more difficult to resolve. For the oxidation of CO and H_2 on NiO, CuO, and Co_3O_4 we believe that the bulk of the evidence points to participation of some—the most active part—of the oxygen on the oxide surface. This conclusion is supported not only by direct experimental data but also by the similarity between the relative activities of the various oxides towards these reactions on the one hand and towards exchange in molecular oxygen on the other hand. For the latter reaction it has been established that oxygen from the surface of the oxides is involved, and that oxygen sorption on the surface of these oxides cannot occur at significant rates to give an atomic form, which has bonding substantially different from the oxygen bond in the surface layer of the crystal lattice of the oxide. The last conclusion follows from the equality of the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the oxide.

It is possible, however, that at lower temperatures and when the surface layer of the oxide shows large departures from its equilibrium oxygen composition, the oxidation will occur through some other form of chemisorbed oxygen, as is the case in the exchange of molecular oxygen on specially activated oxides.

Data on the catalytic oxidation reactions on vanadium pentoxide are still too scanty for unambiguous conclusions. It is possible that the rate of sorption of oxygen and the form of the oxygen bond to the catalyst are substantially altered by the simultaneous adsorption of the compound to be oxidised. This argument, put forward by Roiter[81], is particularly relevant when the adsorption of oxygen and of the oxidisable species is accompanied by electron transfers in opposite directions. There is experimental evidence of a positive effect on the rate of adsorption by preliminary adsorption of another material[82,83].

An extension of the study of the participation of oxygen from the oxides in oxidation reactions, to include a wider range of oxide catalysts and of reactions, would undoubtedly be of interest.

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Studies of the catalysis of isotope exchange in molecular oxygen began relatively recently, and have so far been confined to a limited number of catalysts and a relatively narrow range of reaction conditions. Nonetheless, the results obtained justify the hope that this reaction will prove to be a useful method of studying the mechanism of oxidation reactions, and particularly convenient for characterising the intermediate forms in the interaction between oxygen and solid catalysts.

The most important result obtained so far is the conclusion that exchange in molecular oxygen on the one hand, and isotope exchange with the oxygen of the catalyst (in the case of oxides with an equilibrium oxygen concentration in the surface layer) on the other hand, proceed at equal rates. This equality of rates points to the participation of oxygen from the catalyst in exchange reactions, and also suggests that the oxygen chemisorbed by oxides has the same (or nearly the same) bond energy as the oxygen of the surface layer of the oxide crystal lattice. Hence, the rate of exchange of molecular oxygen can serve as a general characteristic of the reactivity of the oxygen, and can be a useful guide to the rules for the choice of catalysts for oxidation reactions.

The surface oxygen of catalytically active oxides is non-uniform, the degree of non-uniformity being greater, the more active the oxide. There is no simple relationship between the catalytic activity towards exchange and the electronic work function of oxides.

Under the conditions leading to isotope exchange on metals (Pt, Pd, Ag), considerable sorption of oxygen in the surface layer of the metal (equivalent to several monolayers) is observed. In this form, the metals behave very much like oxides towards the catalysis of exchange in molecular oxygen. Platinum is very similar to the most active oxide (Co_3O_4) in the values of the activation energy and of the absolute rate of exchange, and in the nature of the non-uniformity.

The high catalytic activity towards oxygen exchange at low temperatures shown by oxides which have been subjected to strong activation in a vacuum is extremely interesting. The low-temperature activity is short-lived, particularly at high temperatures, and is evidently caused by the departure from equilibrium composition of the oxide brought about by the activation. Isotope exchange with the oxygen of the oxide does not occur under these conditions. Homomolecular exchange on oxides activated in this way involves special intermediate forms of interaction between the oxygen and the catalyst. Studies of the possible role of these forms in the catalysis of oxidation reactions are highly desirable.

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The Electron Spin Resonance Method in Photochemistry

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The electron spin resonance (ESR) method is, at the moment, one of the most sensitive physical methods of detecting, identifying, and studying free radicals, ion-radicals, and molecules in the triplet state formed during photochemical reactions. In this review, the use of the ESR method in studies of photodecomposition and photoionisation reactions of simple and of complex compounds is discussed on the basis of results obtained by Soviet and foreign workers. It is concluded that the ESR method will prove to be a powerful physical method of investigation of photochemical systems only if used in conjunction with other methods (in particular, optical spectroscopy).

CONTENTS

I. Introduction 628
II. ESR studies of photodecomposition reactions 630
1. Photolysis of simple compounds 630
2. Secondary reactions of photogenerated simple free radicals 631
3. Photolysis of complex organic compounds 634
4. Photodecomposition of adsorbed organic compounds 638
5. Photo-ejection of an electron (photoionisation) 638

I. INTRODUCTION

For many years, chemical analysis of the final reaction products has been the most widely used method of investigating the mechanism of photochemical reactions. Knowing the products, one can surmise the nature of the intermediate stages. Methods of separation and of analysis of the reaction products have reached an advanced level of development. For the identification of products, chemists can call on methods such as chromatography, mass spectroscopic analysis, and tracer methods. It is well known that excited states, ions, and free radicals play a key role in photochemical change. If the optical absorption or luminescence spectra of these intermediate states are known, direct identification using the ultraviolet, visible, or infrared bands is possible in principle. However, this approach is often precluded by the extremely short lifetimes of photochemical reaction intermediates.

The difficulty was resolved by Norrish and Porter's publication in 1948 of the impulse photoexcitation method[1] for photo-active systems, in conjunction with fast spectrophotometric measurements, known as the flash spectroscopic or flash photolysis method. Furthermore, studies of the primary stages of photoreactions using the spectra of frozen solutions and mixtures exposed to radiation have increased in scope during the last twenty years. A programme of spectroscopic investigations of chemical reactions at low temperatures was started by Terenin[2,3] as early as in 1940: this was the first attempt to stabilise the intermediates of photochemical reactions in matrices. Subsequently, Lewis and Kasha[4] discovered, in their study of the mechanism of phosphorescence in organic compounds, that free radicals and ion-radicals formed during illumination can be stabilised in rigid, glassy solutions at low temperatures. The main difficulty in this work, pointed out by Frank and Rabinowitch[5], is that the primary products of the photoreaction are often prevented from escaping from their "cage" by the viscosity of the glassy solution, and therefore recombine. On the other hand, the glassy solution must have sufficient rigidity to prevent the active products from diffusing and taking part in secondary, dark reactions. Mixtures of hydrocarbons, alcohols, and ethers at low temperatures are ideal for the purpose: the viscosity of the medium can be controlled either by changing the composition or by changing the temperature of these mixtures.

However, it is sometimes impossible to resolve the optical absorption bands of individual intermediates in photochemical reactions, because they are masked by the absorption bands in the spectrum of the photochemical system due to some of the compounds present in the experimental mixture. If the optical spectrum of the ion or free radical is not known, identification is generally not possible.

Fortunately, photochemical reaction intermediates such as free radicals, ion-radicals, and molecules excited to the triplet state have one important physical property in common: they are paramagnetic due to the presence of unpaired electrons[6]. This makes possible their detection and identification by the electron spin resonance (ESR) method, discovered in 1944 in the Soviet Union by Zavoiskii[7]. Several excellent reviews and monographs on the theoretical and practical aspects of ESR have already been published[8-11], and it is unnecessary therefore to discuss the method in detail. We shall only remark that at the present time this is one of the most sensitive physical methods of detection, identification, and study of free radicals, ion-radicals, and molecules in the triplet (phosphorescent) state.

Hundreds of papers on studies of elementary photoprocesses by the ESR method have been published in the last ten years. As an illustration of the potentialities of the ESR method in photochemistry, we shall consider only a few of these original papers.

The writer has not attempted a detailed analysis of the results quoted in the literature, nor has he concerned himself with matters of purely physical interest. The main emphasis of this review will be a systematic treatment of photochemical investigations by the ESR method. An attempt has been made to preserve the chronological order of the work discussed.

Terenin[12] has given an excellent account of the physical processes underlying the conversion of radiant energy in photochemical systems, and a diagram of the most important photochemical reactions. Following this diagram, we shall classify the photochemical work by the ESR method published up to the time of writing (1966) into the following main photochemical reactions: (1) photodecomposition (photolysis into radicals, photolysis into ions or photoionisation); (2) phototransfer of electrons (photooxidation, photodissociative electron addition); (3) photosensitisation (photosensitised reduction, photosensitised decomposition).

A section on the detection and study by ESR of the triplet (phosphorescent) states of organic compounds has not been included in this review, in spite of its great interest. The omission was deliberate, in order to avoid overloading the article with material which is principally of interest to physicists.

In the main section of this review, we shall discuss the photochemical decomposition of molecules into free radicals and photoionisation processes, investigation by the ESR method.

The first step in any photochemical reaction is the absorption of light by one or more of the components of the photosensitive system under study. Four types of absorption band must be distinguished.

1. Strong ($\lg\epsilon = 3-4$) bands arising from π,π^* absorption in aromatic compounds. These usually occur above 250 mμm, and in conjugated aromatic compounds (dyes) they lie in the visible region of the spectrum. These bands are sharp, and are associated with the transition of one electron from the uppermost filled molecular π-orbital of the ground state to a free non-bonding π^*-orbital of higher energy.

2. Less strong ($\lg\epsilon = 2$) n,π^* absorption bands of heterocyclic compounds, usually in the long-wave part of the absorption spectrum, due to the transition of one of the unshared n-electrons from the hetero-atoms (N, O, S) from a non-bonding $2p$-orbital localised on these atoms to a non-bonding π^* molecular orbital.

3. Strong ($\lg\epsilon = 3-4$), differ σ,σ^* absorption bands of saturated hydrocarbons, found in the ultraviolet region below 200 mμm, due to the transition of an electron from an atomic, bonding σ-orbital to an excited, non-bonding σ^*-orbital (unstable state).

4. Diffuse, long-wave ($\lambda < 260$ mμm) absorption bands from aliphatic alcohols, ethers, amines, alkyl halides, etc. due to the transition of an n-electron to an excited σ^* atomic orbital.

The reactivity of the molecules is determined by the nature of the electronic state, defined by the multiplicity of the state[12] and by the type of electronic transition leading to this state[13-17].

It is known[12] that molecules can exist in the singlet unexcited (ground) state S_0, in a singlet excited state S_1^*, in the lowest (ground) triplet state T_0, and in a triplet excited state T^*. The excited electronic states S_1^*, T_0, and T^* can arise from π,π^*, n,π^*, σ,σ^*, and n,σ^* electronic transitions occurring under the influence of light. The position in energy of these states determines to a large extent the spectral characteristics (absorption and luminescence spectra) and the photochemical properties of the molecules[13-17]. As a rule, the molecules which take part in chemical reactions are not in a singlet S_1^* state, but in the long-lived T_0 state, to which the molecules are transferred by internal conversion[12].

Data on the photochemical action of short-ultraviolet light, which excites the σ,σ^* and n,σ^* transitions in molecules, are so far limited to the photodecomposition and photoionisation reactions of simple molecules in the gas phase, studied by the luminescence of the ejected radicals[18,19] and more recently by flash-photolysis[20] and mass-spectrometrically[21].

However, light absorption is a necessary but not a sufficient condition for the occurrence of a photochemical reaction. After light absorption, a compound does not invariably undergo chemical change, because the excited molecule can undergo physical deactivation processes which involve no chemical conversion[12]. Depending on the spectral composition of the exciting light, the temperature of the medium, and intermolecular interactions, different photoprocesses can take place in a photosensitive reaction system.

The presence of the energy from an absorbed photon in the molecule can manifest itself in several ways. It can: (1) be stored as potential energy of the electronically excited state and either be transferred to another molecule by collision or by exchange or inductive-resonance intermolecular interactions, or else it can be radiated in the form of luminescence; (2) it can be dissipated as heat in a chain of collisions; (3) it can be converted into intramolecular energy of the molecule.

The third way is particularly interesting to photochemists, since under suitable conditions it can lead to dissociation of the molecule into free radicals and ion-radicals. The breaking of chemical bonds in a compound under the influence of light (the photodecomposition reaction) is one of the most direct methods of preparing free radicals.

Since the free radicals formed in most photochemical reactions are very active and undergo secondary chemical interactions, various methods of stabilisation are necessary to enable them to be studied by the ESR method. In the earliest work (1954) on the study of elementary photoprocesses by the ESR method[22,23] the intermediate photoproducts were stabilised in viscous media (in polymer films at room temperature and in frozen solutions). Subsequently, the preferred technique has been the low-temperature stabilisation of the active products in solid solutions.

II. ESR STUDIES OF PHOTODECOMPOSITION REACTIONS

The work of Terenin[18,19], Lewis[24], and Porter[25,26], has produced a substantial fund of spectroscopic data on the photodecomposition of various compounds, which has been responsible for the success of the ESR method. The earliest ESR work was mostly confined to photoreactions whose mechanism had been made clear by the previous work, so that the identification of intermediates involved no difficulties and was a clear proof of the correctness of earlier conclusions.

The first ESR spectra of free radicals formed by ultraviolet irradiation and stabilised in frozen solutions at 77° and 96°K were obtained by Ingram and coworkers[23], who repeated the experiments of Norman and Porter[25] on the photodecomposition of various compounds under the influence of ultraviolet light. Free radical formation was detected by irradiating solid solutions of ethyl iodide, toluene, benzylamine, benzyl chloride, and benzene with light of $\lambda = 254$ mμm. Free radicals appeared also after irradiation of a 40% solution of hydrogen peroxide in water and of the chlorides of oxalato-complexes of tervalent iron in ether–water–alcohol mixtures. The measurements were made on an unsatisfactory ESR apparatus and did not allow accurate identification of the paramagnetic products because the ESR spectra did not show a well resolved hyperfine structure. The photochemical formation of two different free radicals from a single molecule further complicated the identification of the ESR spectra obtained. It was found that the most definite results were obtained from the photodecomposition of hydrogen peroxide by the reaction $H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$. However, more recent work has shown[27-32] that in concentrated aqueous solutions of H_2O_2 ($c > 10^{-2}$ M) the observed ESR spectrum is not due to free OH radicals but to $H\dot{O}_2$ radicals formed by the dark reaction $\dot{O}H + H_2O_2 \rightarrow H\dot{O}_2 + H_2O$.

The doublet ESR spectrum of the $\dot{O}H$ radical could be observed only by irradiating dilute aqueous solutions of H_2O_2 (10^{-2} M or less).[33,34] Stabilisation of the $\dot{O}H$ radical was achieved by minimising the rate of the dark reaction in a dilute solution.

The search for specimens containing active free radicals in measurable concentrations led to the development of the matrix isolation method for these radicals[35]. Solid H_2, Ar, Kr, and CH_4 proved to be suitably inert matrices for stabilising simple free radicals produced photochemically.

1. Photolysis of Simple Compounds

Foner and Cochran[36-38] published a series of researches on the preparation and stabilisation of simple free radicals in these matrices at 4.2°K by ultraviolet irradiation of low-molecular compounds. The source of ultraviolet light was a radio-frequency discharge in a hydrogen tube with a window transparent to ultraviolet (lithium fluoride down to 100 mμm, sapphire to 145 mμm, quartz to 180 mμm, Vycor to 240 mμm). The mixture under study, consisting of the photosensitive material and the matrix gas, was deposited on a sapphire rod at 4.2°K and irradiated with ultraviolet during or after the cooling period, and it was then examined by ESR. Foner and coworkers[38] were able to observe the ESR spectrum of free $\dot{N}H_2$ radicals (triplet of triplets) and $\dot{N}D_2$ radicals (triplet of quintets), produced by photodecomposition in ultraviolet light of 0.5% NH_3 or ND_3 in an Ar matrix at 4.2°K, thus confirming the scheme for the photodecomposition of ammonia first established by Terenin and Neuimin[18]:

$$NH_3 + h\nu \rightarrow \dot{N}H_2 + \dot{H}$$

Some interesting anomalies were observed in the ESR spectrum of the $\dot{N}H_2$ and $\dot{N}D_2$ radicals: whereas the ratio of the hyperfine interaction constants (a_H, a_D) for $\dot{H}$ and $\dot{D}$ is accurately equal to the ratio of the g-factors for their nuclei (6.514), the corresponding constant for nitrogen (a_N) increases only by 15% on going from $\dot{N}H_2$ and $\dot{N}D_2$. The effect is probably associated with differences in the zero-point vibrations of these molecules.

The same workers[36] observed the ESR spectra of hydrogen atoms after ultraviolet irradiation of 1% hydriodic acid in an Ar matrix at 4.2°K. Instead of a single doublet ($I_H = \frac{1}{2}$) with a splitting of 508 Oe, the known ESR spectrum of hydrogen atoms, they found three doublets one of which accurately coincided with the known spectrum.

It is interesting to note that the ESR spectrum of hydrogen atoms obtained by the photodecomposition of water ($H_2O + h\nu \rightarrow \dot{O}H + \dot{H}$) in solid argon at 4.2°K consists of two doublets[39]. The separation of the inner doublets was 507.9 Oe, which is commonly found for condensed $\dot{H}$ atoms and corresponds to a hyperfine splitting constant a_H 0.46% lower than the value for the free hydrogen atom. For the outer doublets the splitting was 516.1 Oe, corresponding to an a_H value 1.5% higher than the free H atom value. As in the previous case, these results were interpreted theoretically[40] as evidence for the penetration of $\dot{H}$ atoms into the available octahedral holes of the face-centred cubic lattice of crystalline argon. Phenomena associated with the capture of $\dot{H}$ atoms at various positions in the

lattice were observed also with krypton and xenon at 4.2°K.

The formation of $\dot{C}H_3$ and $\dot{C}D_3$ radicals was observed by Cochran and coworkers[37] during ultraviolet irradiation of CH_3I and CD_4 respectively in Ar at 4.2°K. The ESR spectrum of the free $\dot{C}H_3$ radical was a quartet of lines with a splitting of 22.9 Oe, $g = 2.0024$, and relative intensities of the components 1 : 3 : 3 : 1, pointing to interaction of the unpaired electron with the protons of three equivalent hydrogen atoms. The $\dot{C}D_3$ radical had a seven-component ESR spectrum ($I_D = 1$) with intensity ratios 1 : 3 : 6 : 7 : 6 : 3 : 1. As was to be expected, the separation of the components of the ESR spectrum was less for the $\dot{C}D_3$ radical than for the $\dot{C}H_3$ radical as required by the ratio of the nuclear g-factors for D and H.

When more complex radicals are trapped in an argon matrix we can no longer average all anisotropic interactions by assuming free rotation in the solid matrix at 4.2°K. With the ethyl radical $CH_3\dot{C}H_2$, obtained by Cochran and coworkers[36] by ultraviolet irradiation of solid 1% ethyl iodide (C_2H_5I) solution in argon at 4.2°K, the ESR spectrum consists of a quartet ($a\beta = 26.3$ Oe) of relatively sharp lines each of which is split into a triplet ($a\beta = 18.5$ Oe) with relatively broad outer components. The sharpness of the lines suggests that the $C_\alpha H_2$ group is free to rotate about the $C_\beta C_\alpha$ bond. The outer lines of each triplet correspond to parallel orientation of the spins of the α-hydrogens, which creates additional magnetic anisotropy. It is not averaged by internal rotations, and therefore line broadening occurs.

Photodecomposition of 1% n-propyl iodide in solid Ar at 4.2°K gave a three-component ESR spectrum for the n-propyl radical C_3H_7. In order to identify the protons responsible for the hyperfine splitting, n-propyl iodide deuterated in the α and β positions was photodecomposed ($CH_3CH_2CD_2I$ and $CH_3CD_2CH_2I$). The authors concluded[36] that the observed ESR spectrum of the n-propyl radical can be explained by assuming that the main contribution to the hyperfine splitting comes from the protons of the two equivalent β-hydrogens.

Cochran and coworkers[39] decomposed SiH_4 by ultraviolet light in Ar at 4.2°K, and obtained an ESR spectrum for the $\dot{S}iH_3$ radicals stabilised under these conditions. The spectrum consisted of a quartet of lines, like that of the $\dot{C}H_3$ radical, but with a somewhat larger separation between the components.

Hayon and Saito[41] used the ESR method to investigate the photodecomposition of HNO_3 in degassed and frozen (77°K) aqueous solutions, for which the following reaction scheme had been proposed[42]:

$$HNO_3 \xrightarrow{h\nu} \dot{O}H + \dot{N}O_2;\ \dot{O}H + HNO_3 \rightarrow H_2O + \dot{N}O_3 .$$

When samples of 0.1, 1.0, and 5.0 M HNO_3 are irradiated with light of $\lambda = 254$ mμm, the solid solution at 77°K develops a blue colour. The ESR spectrum of these coloured samples consisted of the well known[43-48] three-component signal of the $\dot{N}O_2$ radical ($g_\perp = 2.0055$; $g_\parallel = 1.9927$; $A/h = 160$ MHz; $B/h = -8$ MHz), the singlet line of the $\dot{N}O_3$ radical ($\bar{g} = 2.018 \pm 0.001$ and $\Delta H = 10$ Oe), and an additional singlet line with $g = 2.003$. It is interesting to note that yellow light ($\lambda > 480$ mμm) bleaches the samples and leads to the disappearance of the signal with $g = 2.018$. It is known[49-52] that the $\dot{N}O_3$ radical has three absorption bands in the region of 500–700 mμm ($\epsilon = 3000 \pm 1000$ litre mole^{-1} cm^{-1} at $\lambda = 662$ mμm). From energy considerations, the photodecomposition of $\dot{N}O_3$ can be expected to occur by two paths:

$$\dot{N}O_3 \xrightarrow{\lambda > 624\ m\mu m} \dot{N}O + O_2;\ \dot{N}O_3 \xrightarrow{\lambda < 570\ m\mu m} \dot{N}O_2 + \dot{O}.$$

Indeed, the signal of the $\dot{N}O_2$ radical and the singlet line with $g = 2.003$ which had been tentatively assigned to the $\dot{N}O$ radical became more intense in the ESR spectrum after irradiation of the coloured samples with yellow light.

2. Secondary Reactions of Photogenerated Simple Free Radicals

The photochemical formation of simple free radicals in solid matrices at low temperatures is, as stated above, one of the standard methods of investigating primary photoprocesses. The problem of the secondary reactions and subsequent photoconversions of the free radicals at low temperatures is highly relevant on the one hand to the preservation of these radicals by appropriate stabilisation and on the other hand to the realisation of low-temperature reactions involving these radicals.

Pimentel and coworkers[53] observed, in their study of the photodecomposition of HI in solid CO at 20°K, the infrared spectrum of the formyl radical HĊO, apparently produced by the chemical reaction between atomic hydrogen and molecules of the solid matrix according to the scheme

$$HI \xrightarrow{h\nu} \dot{H} + \dot{I};\ \dot{H} + C{=}O \rightarrow H{-}\dot{C}{=}O .$$

Cochran and coworkers[54] showed by the ESR method that the HCO radical is formed in this system even at 4.2°K.

However, this is not the only reaction which can take place at these very low temperatures. It is known that irradiation with vacuum ultraviolet light of 1% HCN in solid argon produces, in addition to the CN radical, a weak ESR signal from the $H_2\dot{C}N$ radical (a triplet of triplets), formed by a secondary dark reaction involving atomic hydrogen:

$$\dot{H} + H{-}C{\equiv}N \rightarrow H_2C{=}\dot{N}.$$

The activity of atomic hydrogen at 4.2°K is demonstrated also by an experiment in which HI mixed with 10% of HCN was photodecomposed in argon at 4.2°K under the influence of light ($\lambda = 254$ mμm). The ESR spectrum of the $H_2\dot{C}N$ free radical, formed by the above scheme, was again observed.

The ESR spectrum of the amino free radical ($\dot{N}H_2$) was observed by Coope and coworkers[55] in the products of the photodecomposition of hydrazoic acid (HN_3) in a krypton matrix at 4.2°K. The first product of the photodecomposition of hydrazoic acid was shown, by a study[56-58] of the optical absorption spectra of the products, to be the imino radical $\dot{N}H$. The $\dot{N}H_2$ radical can be formed by the secondary reaction

$$\dot{N}H + HN_3 \rightarrow \dot{N}H_2 + N_3.$$

In fact, the products of the photodecomposition of hydrazoic acid showed a broad, strong singlet line with $g \simeq 2$, identified as the ESR spectrum of the imino radical, on which the weak nine-component spectrum of the $\dot{N}H_2$ radical was superimposed[38].

As was stated at the beginning of the article, the intermediate products in the photodecomposition of H_2O_2 are $\dot{O}H$ radicals, which are chemically active at 77°K and can extract a labile hydrogen atom from neighbouring molecules of the medium, forming $H\dot{O}_2$ hydroperoxy radicals. Sergeeev and coworkers[32,59-62] have demonstrated the special role of phase transformations in the matrix in determining the reactions of the $\dot{O}H$ and $H\dot{O}_2$ radicals at low temperatures. Depending on the rate at which a 25% aqueous solution of H_2O_2 is cooled, a crystalline or a

glassy phase can be obtained at 77°K. When the samples are irradiated with ultraviolet light, $H\dot{O}_2$ radicals are formed. The destruction of these radicals in a glassy phase does not begin until 143°K, and is complete at 158°K. For aqueous solutions of H_2O_2 this temperature is the glass–crystal phase transition point. The destruction of the $H\dot{O}_2$ radicals is probably caused by the increased mobility of the molecules during the phase transition. In crystalline samples there is no destruction of the radicals at 158°K. On raising the temperature from 163° to 183°K a stepwise disappearance of the radicals was observed, corresponding to the loss of a definite fraction of the radicals at a number of specific temperatures. Complete destruction of the radicals does not occur until the temperature reaches 220°K, the melting point of the eutectic mixture.

A similar type of destruction of the radicals was observed by the same authors for the phase transition point at 103°K in their work on the photolysis of H_2S frozen at 77°K.

More recently, several interesting features of the photolysis of dilute aqueous solutions of H_2O_2 have been reported. Thus, at H_2O_2 concentrations below 10^{-3} M the ESR spectrum consists of the combined signals from the $\dot{O}H$ and $H\dot{O}_2$ radicals[33,34]. On increasing the time of irradiation the ESR signal from $H\dot{O}_2$ decreases. The observed change in the concentration of the radicals can be explained by the following series of reactions:

$$H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$$
$$\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2$$
$$H\dot{O}_2 \xrightarrow{h\nu} \dot{H} + O_2 \cdot$$

It is usually assumed that the formation of the hydroperoxy ($H\dot{O}_2$) radicals is due to the diffusion of $\dot{O}H$ at 77°K during the dark period. However, Sergeev and coworkers consider[61] that diffusion of $\dot{O}H$ in ice at 77°K is unlikely, and they explain the formation of $H\dot{O}_2$ in dilute aqueous solutions of H_2O_2 by postulating migration of the free valency along the system of hydrogen bonds

$$\begin{array}{ccccccccccccc} O\cdots(H-O\cdots H-O)_n\cdots H-O & \rightarrow & O-H\cdots(O-H\cdots O-H)_n\cdots O \\ | & & | & & | & & | & & | & & | & & | \\ H & & H & & H & & O-H & & H & & H & & O-H \end{array}.$$

According to this scheme, any disturbance of the hydrogen bond structure should lead to stabilisation of the $\dot{O}H$ radical. Stabilisation of this radical can therefore be expected in solutions with a high concentration of H_2O_2. This expectation was confirmed[62], but not in a pure aqueous solution: addition of sodium perchlorate (8 M) was necessary to destroy the hydrogen bond structure of the water. Ultraviolet irradiation of such a solution produced ESR signals from the $\dot{O}H$ radical. In the absence of sodium perchlorate, photodecomposition of aqueous solutions of H_2O_2 produced only $H\dot{O}_2$ radicals. This is a clear confirmation of the proposed migration of free valencies along the system of hydrogen bonds.

The chemical activity of hydroxyl radicals produced by the photodecomposition of hydrogen peroxide at 77°K or 96°K was successfully applied by Ingram and coworkers[63-69] to the preparation of free radicals from various aliphatic alcohols and saturated hydrocarbons. The ESR spectra obtained by ultraviolet irradiation (λ = 365 or 254 mμm) of frozen hydrogen peroxide solutions (10^{-1}–10^{-6} M) in various readily oxidisable solvents were due to free radicals of the solvent molecules which had been dehydrogenated by the free hydroxyl. Thus, the reaction of $\dot{O}H$ with methanol[65] at 96°K produces an ESR spectrum consisting of three components with an intensity ratio of 1 : 2 : 1, showing that the hyperfine structure of the ESR spectrum arises from the interaction of an unpaired electron with the protons of two equivalent hydrogen atoms and is due to the $\dot{C}H_2OH$ radical. Several characteristic ESR spectra for various alcohols were obtained in this way, ranging from methanol to n-hexanol (including some secondary and tertiary alcohols). Using deuterated alcohols it was shown that the $\dot{O}H$ radical removes the α-hydrogen from the alkyl group and that the proton of the hydroxyl group of the alcohol does not interact with the unpaired electron of the radical.

Shelimov and coworkers[70,71] studied by the ESR method the kinetics of the accumulation, disappearance, and transformation of the radicals formed by ultraviolet irradiation of dilute H_2O_2 solutions in CH_3OH and C_2H_5OH at 77°K. When solutions of H_2O_2 in CH_3OH at 77°K are irradiated with light from a SVDSh-250 mercury lamp ($\lambda < 320$ mμm), an ESR spectrum appears after a few minutes, and is found to consist of the combination of the spectra of two free radicals: $\dot{C}H_3$ and $H\dot{C}O$.[70] Under prolonged irradiation the concentration of these radicals reach a limiting value. When the light is removed the form of the ESR spectrum begins to change: the intensity of the lines from the $\dot{C}H_3$ radical decreases, and at the same time the three-line ESR signal of the $\dot{C}H_2OH$ radical appears in the spectrum and begins to grow. After a second exposure to light the concentration of $\dot{C}H_2OH$ falls off quickly, with a corresponding increase in the concentration of CH_3 radicals. Meanwhile, the concentration of $H\dot{C}O$ remains practically unchanged. It should be noted that a kinetic picture very similar to the above was obtained when a solution of C_6H_6 in CH_3OH was irradiated at 77°K. The photochemical behaviour of these systems can be described by the following scheme:

$$H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$$
$$(C_6H_6 \xrightarrow{h\nu} C_6H_6{}^*)$$
$$\dot{O}H\,(C_6H_6{}^*) + CH_3OH \rightarrow H_2O\,(C_6H_6 + \dot{H}) + \dot{C}H_2OH$$
$$\dot{C}H_2OH \xrightarrow{h\nu} :CH_2 + \dot{O}H \xrightarrow{+CH_3OH} \dot{C}H_3 + 2\dot{C}H_2OH + H_2O$$
$$\searrow H\dot{C}O + H_2$$
$$\dot{C}H_3 + CH_3OH \rightarrow CH_4 + \dot{C}H_2OH\,.$$

The formyl radical ($H\dot{C}O$) is known to have absorption bands in the visible region of the spectrum[72]. If the irradiation is repeated with light of $\lambda > 320$ mμm, a very fast decrease in the concentration of the $H\dot{C}O$ radical is observed, due to the photodecomposition of this radical with formation of the $\dot{C}H_2OH$ radical according to the scheme

$$H\dot{C}O \xrightarrow{h\nu} \dot{H} + CO;$$
$$\dot{H} + CH_3OH \rightarrow H_2 + \dot{C}H_2OH.$$

After the concentration of $H\dot{C}O$ radicals has fallen to zero the concentration of $\dot{C}H_2OH$ no longer increases. A mass spectroscopic analysis of the gaseous products of the photodecomposition of H_2O_2 in CH_3OH detected H_2 (57%), CO (26%), and CH_4 (17%).

It follows from this sequence of experimentally identified elementary steps that a photochemical system irradiated with the unfiltered light from a SVDSh-250 mercury lamp will undergo a peculiar type of chain reaction involving the decomposition of methanol at 77°K with photochemical acts of chain initiation and branching and with some chain propagation steps.

Shelimov and coworkers[71] also investigated by ESR the kinetics of the accumulation, disappearance, and mutual conversion of the radicals formed during irradiation by ultraviolet light (λ = 240 mμm) of H_2O_2 or C_6H_6 solutions

in ethanol at 77°K. The solutions were thoroughly degassed before photodecomposition. As in the case of the methanolic solutions discussed above, the form of the ESR spectra and all the kinetic characteristics were the same for the two solutes. The formation of the following radicals was recorded: $\dot{C}_2H_5$, $\dot{C}H_3$, $CH_3\dot{C}HOH$, and $CH_3CH_2\dot{O}$. It was shown that under the action of ultraviolet light of specific wavelengths ($\lambda > 360$ mμm) the alcoholic radicals $CH_3\dot{C}HOH$ decompose with formation of alkyl radicals ($\dot{C}_2H_5$ and $\dot{C}H_3$). When the light is removed, a gradual disappearance of the alkyl radicals is observed at 77°K, accompanied by the appearance of the radicals $CH_3\dot{C}HOH$ and $CH_3CH_2\dot{O}$ (singlet ESR line, $\Delta H = 14$ Oe). It is found that the $CH_3CH_2\dot{O}$ radicals isomerise under the action of light with $\lambda > 360$ mμm to give $CH_3\dot{C}HOH$ radicals. From mass spectroscopic data, the main gaseous products of the photodecomposition of H_2O_2 solutions in C_2H_5OH are CO (23%), CH_4 (19%), and H_2 (58%). Evidently, a very important stage in their formation is the decomposition of the alcoholic radicals under the influence of light to give alkyl radicals.

Mal'tsev and Petrov[73,74] have shown that the ESR spectra of the photodecomposition products of hydrogen peroxide in tertiary alcohols of general formula $R(CH_3)_2COH$, where $R = CH_3$, C_2H_5, $CH_2{=}CH$, $HC{\equiv}C$, consist of a combination of components associated with the alcoholic radical $R(CH_3)C(\dot{C}H_2)OH$ and the CH_3 radical. The formation of t-butanol radicals during photodecomposition of hydrogen peroxide in this alcohol had previously been reported by Ingram and coworkers[63] and by Symons and coworkers[68]. Mal'tsev's paper describes[74] the mechanism of the photoprocesses occurring in solid solutions of H_2O_2 in tertiary alcohols taking trimethylmethanol as an example. The ESR spectrum obtained after irradiation with the unfiltered light from a DRSh-500 mercury lamp contains 7 lines which can be assigned as a triplet for the alcoholic radical and a quartet for the methyl radical. Storage of the sample, after irradiation at 77°K, for 60–70 h in the dark is accompanied by gradual disappearance of the components of the quartet and growth of the triplet. When a frozen solution of H_2O_2 in trimethylmethanol is irradiated with light of wavelength 340–390 mμm the ESR signal consists of the triplet only. However, the quartet spectrum of the CH_3 radical appears after further irradiation, with light of $\lambda < 320$ mμm, of a solution in which the concentration of alcoholic radicals (triplet ESR spectrum) is below the maximum. The following reaction scheme can be proposed for this system:

$$H_2O_2 \xrightarrow{u.v.} 2\dot{O}H$$

$$(CH_3)_3COH + \dot{O}H \rightarrow (CH_3)_3C(\dot{C}H_2)OH + HOH$$

$$(CH_3)_3C(\dot{C}H_2)OH \xrightarrow{u.v.} \dot{C}H_3 + CH_3\overset{\|}{C}CH_3 \,.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$

But the authors[74] suggest the following mechanism

$$(CH_3)_3COH + \dot{O}H \rightarrow (CH_3)_3C\dot{O} + HOH$$

$$(CH_3)_3C\dot{O} \xrightarrow{u.v.} \dot{C}H_3 + CH_3\overset{\|}{C}CH_3 \,.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$

on the grounds that appreciable concentrations of methyl radicals appeared only in samples which after storage in the dark at 77°K showed a singlet ESR line in the centre of the spectrum, tentatively ascribed to the radical $(CH_3)_3C\dot{O}$.[75] The authors postulate that the penultimate reaction is caused by "hot" OH radicals which appear only under the influence of ultraviolet light with $\lambda < 340$ mμm.

Quite recently, Livingston and Zeldes[76] have used the ESR method to study the reaction of photogenerated ȮH radicals with alcohols in the temperature range from −70° to +60°C. Using a concentrated beam of ultraviolet light, they irradiated a flow of alcohol containing 1% of H_2O_2 in the cavity of their radio-frequency spectrometer. This technique allowed them to produce measurable steady-state concentrations of short-lived radicals. In the absence of dissolved oxygen the main reaction products were the radicals formed by the removal of the α-hydrogen from a molecule of the alcohol by the hydroxyl radical. The RĊHOH radicals, where R = H, CH_3, C_2H_5, C_3H_7, $(CH_3)_2CH$, and C_6H_5, had hyperfine splitting constants a_α in the range 14.7–17.4 Oe, and $g = 2.00298$–2.00334. For the alcoholic radicals with β-hydrogens, $a_\beta = 20.0$–22.2 Oe. The ring protons of the benzyl alcohol free radicals were found to be non-equivalent. Removal of the α-hydrogen from allyl alcohol by a free hydroxyl produces two geometrically isomeric free radicals of the alcohol.

Norman and Porter[77] found that solutions of iodine in ether–isopentane–ethanol (EPA) mixtures at 77°K are decolorised by visible light. When the irradiated solutions are allowed to warm up, the colour of the iodine is restored, indicating stabilisation of iodine atoms at 77°K. Filseth and Willard[78] investigated the processes involved in the bleaching of these solutions, and possible chemical reactions between iodine and saturated solvent molecules, by applying optical spectroscopy and ESR to solutions of iodine in EPA, and also in ethanol, ether, and isopropanol at 90° and 77°K before and after irradiation (AN-6-1000 W), and also after thawing the system to room temperature. Spectrophotometric measurements on solutions irradiated at 90°K showed strong absorption at 291 and 358 mμm, due to tri-iodide, which disappeared at room temperature whilst the absorption bands of molecular iodine reappeared. The ESR spectra of iodine solutions irradiated at 77°K indicate that the iodine atoms produced by the photodissociation of molecular iodine can extract an α-hydrogen atom from the solvent molecule with formation of alcoholic radicals. Hydrogen removal by an iodine atom in the ground state has a low probability at 77°K, because the process is endothermic and requires an energy of the order of 20–30 kcal. The most probable reaction mechanism is the following

$$I_2(^1\Sigma_g) \xrightarrow{h\nu} I_2(^3\Pi) \rightarrow \dot{I}(^2P_{3/2}) + \dot{I}(^2P_{1/2})$$

$$\dot{I}(^2P_{1/2}) + RH \rightarrow HI + \dot{R}$$

$$\dot{I} + I_2 \rightarrow I_2 \cdots \dot{I}$$

$$I_2 \cdots \dot{I} + \dot{I} \rightarrow 2I_2 \,.$$

In order to arrive at a more complete understanding of low-temperature reactions of the type $\dot{X} + RH \rightarrow \dot{R} + HX$, where X is a halogen atom, and to explain the features of the photodecomposition of mixtures of halogens and aliphatic organic compounds, Sergeev and coworkers[62] studied the formation of free radicals during ultraviolet irradiation of mixtures of bromine (or chlorine) with various hydrocarbons and alcohols at 77°K. These included chlorine and bromine mixtures with iso-octane, isopentane, pentane, and cyclohexane. Radicals were formed only in the mixtures with chlorine when irradiation was with ultraviolet light of $\lambda > 280$ mμm. From the number of components of the hyperfine structure and their separation, the ESR spectra can be assigned to radicals of the type $(CH_3)_2\text{–}\dot{C}\text{–}CH_2\text{–}CH_3$ and $\dot{C}_6H_{11}$, formed by the reaction

$$Cl_2 + RH \xrightarrow{h\nu} 2\dot{C}l + RH \rightarrow HCl + \dot{R} \,.$$

The absence of radicals in the Br_2 mixtures can be ascribed to the strong endothermicity of these reactions, which do not readily occur at 77°K.

Ultraviolet irradiation ($\lambda > 280$ mμ) of mixtures of chlorine or bromine with methanol, ethanol, and isopropanol produced complex ESR signals, consisting of several free radical spectra superimposed. These radicals were formed by secondary photodissociation of the radicals formed in the primary process. Essentially, the processes observed in the photodecomposition of H_2O_2 in alcohols occur also in these systems. However, the activation energy of the reaction $\dot{B}r + RH_\alpha OH \rightarrow HBr + \dot{R}OH$ is ~ 9 kcal mole^{-1} in the case of methanol[79], and therefore the removal of an α-hydrogen atom from a molecule of the alcohol has a low probability at 77°K. According to Sergeev[62,80], the formation of organic free radicals in the alcohol–halogen system involves molecular charge-transfer complexes between the halogen and the oxygen of the alcohol formed in the condensation, which alter, the absorption spectrum of the system. The following mechanism is proposed for the formation of the radicals: light absorption causes excitation of the complex and transfer of an electron from the oxygen of the alcohol to the bromine, followed by the formation of the $R\dot{H}O$ radical which isomerises to $\dot{R}OH$ under the influence of light.

3. Photolysis of Complex Organic Compounds

Piette and Landgraf[75] have successfully applied the ESR method to studies of the photodecomposition of primary, secondary, and tertiary butyl hydroperoxides of structure R–O–O–H, where R = $CH_3CH_2CH_2CH_2$ (primary), $CH_3CH_2\dot{C}HCH_3$ (secondary), and $-C(CH_3)_3$ (tertiary). The source of ultraviolet light was a medium-pressure mercury lamp (N85S3). From energy considerations, breaking of the O–O bond with formation of alkoxy and hydroxyl radicals could be expected under the influence of light. For the alkoxy radical $R\dot{O}$, the density of the unpaired electron can be expected to have a low value on the α-protons and a negligible value on the β-protons, because of the influence of the oxygen atom. Hence, the ESR spectrum of these radicals should show a triplet, a doublet, and a singlet for primary, secondary, and tertiary butyl hydroperoxide respectively. In all cases the hyperfine splitting constant a_H should lie between 2 and 3 Oe. Piette found a triplet ESR signal after light irradiation of primary butyl hydroperoxide, a doublet with secondary butyl hydroperoxide, and a singlet with the tertiary compound, the splitting being 3.5 and 2.8 Oe respectively. Thus, it was shown that the photodecomposition of butyl hydroperoxides goes through the formation of alkoxy radicals. The ESR spectrum of the hydroxyl radical $\dot{O}H$ was not detected, probably because of its short lifetime.

Piette[81] studied the photodecomposition of simple aliphatic alcohols during irradiation with unfiltered ultraviolet light. Irradiation of methanol at 77°K gave an ESR signal consisting of two superimposed spectra: a quartet of lines from the $\dot{C}H_3$ methyl radical and a doublet of lines with a splitting of about 120 Oe from the $H\dot{C}O$ radical. On irradiation of methanol which had been deuterated in the hydroxyl position (CH_3OD), the ESR signal was the same as with ordinary methanol. Irradiation of CD_3OH led to the appearance of a seven-line spectrum from the $\dot{C}D_3$ radical and an unresolved multiplet. The doublet with a splitting of 120 Oe was not obtained in this case. Irradiation of ethanol gave rise to a complicated ESR spectrum. As shown by Sullivan and Koski[82–84], and by Shelimov and coworkers[70,71], these free radicals stabilised at 77°K are the result of interdependent, complex photochemical reactions of alcohols, so that primary photoprocesses in these materials can be assessed only by spectral and kinetic studies at different temperatures.

Maas and Volman[85] studied the action of ultraviolet light on various pure allyl alcohols (allyl alcohol, but-2-en-1-ol, but-1-en-3-ol) at 77°K, and found that the primary photochemical act for these compounds is the breaking of the C–O bond with formation of the corresponding allylic hydrocarbon free radicals. These radicals are stable at 77°K. However, at higher temperatures (100–130°K) hydroxy-allyl radicals appear with the allyl hydrocarbon radicals: they are formed by the removal of an α-hydrogen from the alcohol by the active hydroxyl radical produced in the primary photochemical act (photodissociation of the C–O bond).

Ultraviolet irradiation of 2-hydroxy-2-methylbut-1-ene, which does not contain α-hydrogen, gives rise to the ESR spectra of the $\dot{C}H_3$ and $R\dot{C}H_2$ radicals, probably formed in the primary process.

Poole and Anderson[86] reported the observation of the ESR spectra of radicals, stable at 77°K, formed by ultraviolet irradiation of normal and branched unsaturated hydrocarbons (alkenes). Their light source was a high-pressure mercury lamp (GE-BH6), producing a flux of 16.9 W steradian^{-1} in the photochemically active wavelength range (250–380 mμ). The following compounds were irradiated with ultraviolet: methylacetylene (propyne), pent-2-ene (2-amylene), hex-1-ene and hex-2-ene, hept-2-ene, oct-1-ene and oct-2-ene, and also 3-ethylpent-2-ene, 3-methylbut-2-ene, 2,4,4-trimethylpent-2-ene, 4-methylpent-2-ene, and 2,6-dimethylhept-3-ene. The model used to interpret the observed ESR spectra assumed the absorption of a photochemically active photon by the chromophoric group of the molecule, followed by dissociation into two fragments. The light fragment (hydrogen atom, or methyl radical), being able to diffuse at 77°K, reacts with neighbouring species. The heavy fragment is stabilised at 77°K and is responsible for the ESR signal in every case. The hyperfine structure of the ESR signal results from the interaction of the unpaired electron with the protons of the hydrogen atoms in the α and β positions. However, Anderson and Beasley[87] subsequently showed that the appearance of free radicals in ultraviolet-irradiated alkenes is initiated by the photodecomposition of organic peroxides[88] present as impurities in the alkenes used for the investigation:

a)
$$ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H$$
$$R\dot{O} + R'H \rightarrow ROH + \dot{R}'$$
$$\dot{O}H + R'H \rightarrow HOH + \dot{R}'$$

b)
$$R\dot{O} + C{=}C{-}C{-}R' \rightarrow RO{-}C{-}\dot{C}{-}C{-}R'$$
$$\dot{O}H + C{=}C{-}C{-}R' \rightarrow HO{-}C{-}\dot{C}{-}C{-}R' .$$

Kuwata and Hirota[89] investigated the photodecomposition of organic ketones (acetone and benzophenone) by the ESR method. Several types of free radical could have been expected[90] in the photodissociation of acetone, namely

$$CH_3COCH_3 \xrightarrow{h\nu} CH_3\dot{C}O + \dot{C}H_3$$
$$CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO .$$

However, several hours' irradiation of pure acetone with ultraviolet light at 77°K did not produce a detectable amount of free radicals. A single ESR line with ΔH = 30 Oe and g = 2.003 was observed by irradiating a solution

of acetone in alcohol or in EPA mixture (ether–isopentane–alcohol), but the authors were unable to identify the radical responsible for this line. A singlet ESR spectrum (ΔH = 23–24 Oe, g = 2.003) was obtained after ultraviolet irradiation of pure benzophenone or a solution of benzophenone in ethanol or EPA at 77°K. As in the previous case, it was not possible to identify the free radicals.

In a recent investigation by Pukhal'skaya and coworkers[91] on the photoconversions of radicals in γ-irradiated frozen acetone, the photodissociation of acetone frozen at 77°K and of a 50% aqueous solution of acetone were also examined in control experiments. The light source was a DRSh-500 super-high pressure mercury lamp. The ESR signal obtained consisted of two superimposed spectra: the spectrum of the $\dot{C}H_3$ radical (a quartet of lines with intensity ratio 1 : 3 : 3 : 1) and that of the acetyl radical $CH_3C\dot{O}$ (singlet line). The authors point out that the rate of appearance of $\dot{C}H_3$ radicals, assessed from the initial portion of the kinetic curve for the accumulation of these radicals during illumination, is higher by a factor of two than the rate of appearance of acetyl radicals: this seems to be further confirmation of the generally accepted scheme for the photodecomposition of acetone. The assignment of the singlet in the ESR spectrum to the acetyl radical raises some doubt. The unpaired electron of the $CH_3\dot{C}O$ radical can interact with the protons of three methyl hydrogens, leading to an ESR spectrum consisting of four equidistant components with a binomial intensity distribution, 1 : 3 : 3 : 1. Such a spectrum was in fact obtained by Morton and Falconer[92] in the photodecomposition of biacetyl $(CH_3CO)_2$ at 77°K in a vacuum using a low-pressure mercury lamp. After 90 min irradiation the spectrum consisted of two superimposed quartets, one of which had a hyperfine splitting of 66 ± 5 MHz and g = 2.0027 ± 0.0008 and could be assigned to the methyl radical, the second having 47 ± 5 MHz and g = 2.0055 ± 0.0008 and arising, according to the authors, from the acetyl radical. The signal from the methyl radical fell in intensity by a factor of 2 in 15 min after the irradiation ceased; on the other hand, the signal from the acetyl radical did not change in the dark at 77°K, but on raising the temperature to 140°K it rapidly disappeared without changing shape. The authors point out that the initial concentration of methyl radicals was about 5 times higher than the concentration of acetyl radicals, which can be explained by two photoreactions occurring consecutively:

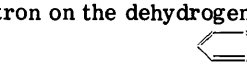
$$CH_3COCOCH_3 \xrightarrow{h\nu} 2CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO.$$

The formation of methane by the photodissociation of methyl iodide and of azomethane in a hydrocarbon solvent[50] at 77°K also suggested that the abstraction of a hydrogen atom by a methyl radical by the reaction $\dot{C}H_3 + RH \rightarrow CH_4 + \dot{R}$ proceeds at appreciable rates at low temperatures. To confirm the accepted views on this type of reaction, Varbanskaya and coworkers[93] made an ESR study of the photodissociation of azomethane and methyl iodide, and also of acetone and acetaldehyde in methylcyclohexane at 77°K under the influence of ultraviolet light of various wavelengths. In the first two cases the ESR spectrum showed the methylcyclohexyl radical ($\dot{R}$), formed by the removal of a hydrogen atom by a $\dot{C}H_3$ free radical from the methylcyclohexane molecule. Four narrow components of different intensity with a splitting of ~ 23 Oe and intensity ratio 1 : 3 : 3 : 1 can be resolved in the ESR spectrum, pointing to the formation and stabilisation of methyl radicals under these conditions. The results justify the conclusion that methyl radicals are undoubtedly formed during the photolysis of CH_3I and $CH_3N_2CH_3$ in the solid phase at 77°K: depending on the wavelength of the active light, they can recombine immediately after formation in the "cage" or they can enter into replacement reactions, or again they can be stabilised and emerge from the cage. It was found that methyl radicals formed by the photodissociation of methyl iodide at 77°K retain their activity also towards unsaturated compounds of the olefin type. These radicals can either add on to olefins at the double bond or they can extract a hydrogen atom from the methylene group, leading to the formation of alkyl or allyl radicals respectively, as can be verified by the ESR method[94].

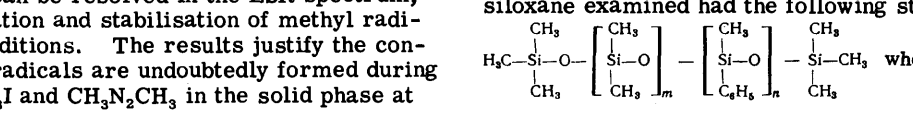
Bielski and Timmons[95] studied the photodecomposition of aliphatic nitro-compounds (nitromethane, methyl nitrite, tetranitromethane) at 77°K. Brief irradiation (from 5 s to several minutes) of these compounds with ultraviolet light from a GE-BH6 high-pressure lamp or a low-pressure lamp led to the appearance of complex ESR signals corresponding to a number of superimposed ESR spectra from different radicals. In particular, after irradiation of a solution of nitromethane in water or in CCl_4 the observed ESR signal can be interpreted, in accordance with the photoreaction scheme $CH_3NO_2 \xrightarrow{h\nu} \dot{C}H_3 + \dot{N}O_2$, as the combination of a quartet of narrow lines from the $\dot{C}H_3$ radical and a triplet of asymmetric lines from the $\dot{N}O_2$ radical. When the solution temperature is raised from 77 to 193°K the methyl radical spectrum disappears and only the $\dot{N}O_2$ radical spectrum remains. A poorly resolved ESR signal was obtained from photodecomposition of methyl nitrite (CH_3ONO). According to the photodissociation scheme proposed by Gray and Style[96], $CH_3ONO \xrightarrow{h\nu} CH_3\dot{O} + \dot{N}O$, the ESR spectrum of the methoxyl group and of $\dot{N}O$ would have been expected. Indeed, the central singlet line can be assigned to the methoxy radical[82]. However, when the temperature of the sample is raised to 193°K, there only remains the ESR spectrum characteristic of the $\dot{N}O_2$ radical, whose appearance is difficult to explain. The photodecomposition of tetranitromethane at 77°K invariably led, irrespectively of the matrix (water, or methanol), to a single ESR spectrum: that of the $\dot{N}O_2$ radical, whose formation can be described by the scheme $C(NO_2)_4 \xrightarrow{h\nu} \dot{C}(NO_2)_3 + \dot{N}O_2$. No spectrum was obtained from the $\dot{C}(NO_2)_3$ radical, probably because of strong interaction with the matrix.

The action of ultraviolet light (SVDSh-1000) on alkylphenylacetylenes (methylphenylacetylene, deuteromethylphenylacetylene, ethylphenylacetylene) produces an intense ESR spectrum pointing to the localisation of the unpaired electron on the dehydrogenated alkyl group[97]:



Irradiation of dialkylacetylenes (R–C≡C–R) produces complicated ESR spectra, probably due to the interaction of the unpaired electron with all the protons of the alkyl groups as a result of the delocalisation of this electron over the whole of the molecule. Thus, in compounds of the type of R–C≡C–Ar and R–C≡C–R (R = CH_3, C_2H_5), the formation of free radicals is due to the photo-removal of a hydrogen atom from the alkyl groups of the substituted acetylenes.

Voevodskii, and Bubnov and coworkers[98,99], have successfully applied the ESR method to the characterisation of the elementary processes of formation and of reaction of free radicals in irradiated organosilicon compounds (polyphenylmethylsiloxane, silazanes). The polyphenylmethylsiloxane examined had the following structure[98]:



where m = 18–20, n = 5–7.

Ultraviolet irradiation of this compound with condensed light from a DRSh-500 super-high pressure mercury lamp at 77°K produces a well resolved ESR spectrum in which two groups of lines with hyperfine structure can be distinguished: (1) a quadruplet with a splitting of 24 ± 0.5 Oe and intensity ratio 1 : 3 : 3 : 1, and 2) a triplet with a splitting of 21 ± 0.5 Oe and intensity ratio 1 : 2 : 1. On the basis of these findings, the authors conclude that ultraviolet irradiation of polyphenylmethylsiloxane gives rise to the radicals $\dot{C}H_3$ and $-O-\overset{\overset{CH_2}{|}}{\underset{\underset{R}{|}}{Si}}-O$, where R = CH_3, C_6H_5. On interrupting the irradiation the spectrum of the methyl radical gradually disappears, with a simultaneous increase in the intensity of the spectrum of the second radical according to the scheme

$$\dot{C}H_3 + R-CH_3 \xrightarrow{k_1} CH_4 + R-\dot{C}H_2 \quad (k_1 = 3.5 \cdot 10^{-6}\ s^{-1})$$

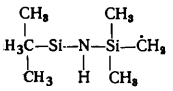
$$\dot{C}H_3 + \dot{C}H_3 \xrightarrow{k_2} C_2H_6 \quad (k_2 = 1.2 \cdot 10^{-21}\ cm^3\ s^{-1}) .$$

In addition to methyl radicals, irradiation should produce radicals with an unpaired electron on the silicon atom, $-\dot{Si}-$. Since these are not manifest in the ESR spectrum, it can be suggested that they disappear under the conditions of the experiment by a fast process whose mechanism is not clear. The kinetics of the accumulation of free radicals were studied as a function of the intensity (I) of the incident light. At low intensities of incident light the initial rate of accumulation of CH_3 radicals was found to be proportional to I^2, and the initial rate of formation of $R-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{Si}}-\dot{C}H_2$ radicals was proportional to I over the whole of the experimental range of ultraviolet light intensities. This led to the conclusion that the formation of one methyl radical requires the successive (two-stage) absorption of two photons. The absorption of the first photon ($\lambda \leqslant$ 300 mμm) breaks the $\rangle Si-CH_3$ bond, but the radical remains within the "cage". Only the absorption of a second photon ($\lambda \geqslant$ 350 mμm) results in the appearance of a free $\dot{C}H_3$ radical.

However, the formation of $R-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{Si}}-\dot{C}H_2$ radicals can apparently occur also by direct removal of a hydrogen atom from the methyl group following the absorption of a quantum of ultraviolet light by the polyphenylmethylsiloxane molecule.

In keeping with the results obtained by the ESR method, a mass spectrometric analysis of the gaseous end-products of the photodecomposition of polyphenylmethylsiloxane found 70% of methane, 5% of ethane, and 25% of hydrogen.

The ESR method has been used in conjunction with a mass spectrometric analysis of the gaseous end-products also to investigate the photoreactions of the following silazanes: (1) hexamethyldisilazane $(CH_3)_3SiNHSi(CH_3)_3$; (2) hexamethylcyclotrisilazane $[(CH_3)_2SiNH]_3$; (3) octamethylcyclotetrasilazane $[(CH_3)_2SiNH]_4$; (4) trimethylcyclotrimethylsilazane $[(CH_3)HSiNCH_3]_3$; (5) tetramethylcyclotetramethylsilazane $[(CH_3)HSiNCH_3]_4$. These compounds show remarkable absorption in the wavelength region below 300 mμm. Ultraviolet illumination of compound (1) at 77°K gives a well resolved ESR signal consisting of seven hyperfine structure lines from two superimposed ESR spectra: a quadruplet with a splitting of 24 ± 0.5 Oe ($\dot{C}H_3$) and a triplet with a splitting 21 ± 0.5 Oe from the radical



The ESR results justify the assertion that photolysis of compound (1) at 77°K follows essentially the same path as the photolysis of polyphenylmethylsiloxane, i.e.

$$M \xrightarrow{h\nu} \begin{cases} \rightarrow \equiv \dot{Si} + \dot{C}H_3 \\ \rightarrow \dot{H} + R\dot{C}H_2 \end{cases}$$

$$\dot{H} + M^{**} \rightarrow H_2 + R\dot{C}H_2$$

$$\dot{C}H_3 + M \rightarrow CH_4 + R\dot{C}H_2$$

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6 .$$

Components from the radicals $\dot{C}H_3$ and $R\dot{C}H_2$ can be found also in the ESR spectra of compounds (2) and (3) irradiated with ultraviolet light at 77°K. However, the ESR spectrum is distorted by the presence of a broad, asymmetric line from the peroxy radical produced by a reaction between the molecular oxygen entrained in the structure of these compounds and the radicals formed by irradiation. Ultraviolet irradiation of compound (4) gives an ESR signal consisting of a broad symmetrical line superimposed on a triplet with a splitting of 21 ± 0.5 Oe from the $R-\dot{C}H_2$ radical. The singlet line is apparently due to the formation under the influence of ultraviolet of a radical with an unpaired electron on the silicon atom[100]. These results showing the type of photogenerated free radicals, combined with data on the composition of the gaseous photolysis products, allow the following scheme to be put forward for the radical processes in compound (4):

$$M \xrightarrow{h\nu_1,\ I_a} \dot{H} + \rangle\dot{Si}$$

$$\dot{H} + M \xrightarrow{k_1} H_2 + R\dot{C}H_2$$

$$\dot{H} + R\dot{C}H_2 \rightarrow M$$

$$\rangle\dot{Si} + \dot{Si}\langle \rightarrow \rangle Si-Si\langle$$

$$M \xrightarrow{h\nu_1,\ \beta I_a} \dot{C}H_3 + \rangle\dot{Si}$$

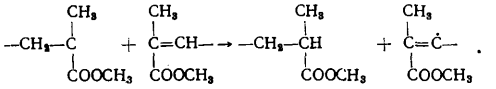
$$\dot{C}H_3 + M \rightarrow CH_4 + R\dot{C}H_2 .$$

Ultraviolet irradiation of compound (5) gave rise to an ESR spectrum similar to the previous one, its only distinguishing feature being that the singlet signal was significantly stronger than in compound (4). From the kinetics of the accumulation of free radicals, in conjunction with the composition of the gaseous products of the photodecomposition of (5), it was concluded that under the influence of ultraviolet light compound (5) undergoes the same processes as compound (4), but the breaking of the $\rangle Si-C$ and $\rangle Si-H$ bonds is more efficient, and the rate of reaction of $\dot{H}$ with silazane (5) is greater. This conclusion is in keeping with chemical considerations of the decreased stability of cyclosilazanes with increase in molecular chain length.

The photodecomposition of the hydroperoxide of atactic polypropene was investigated by Ershov[101] using the ESR method. This worker attempted a quantitative assessment of the rate of photodecomposition of the hydroperoxide obtained by thermal oxidation of polypropene, to give a concentration of hydroperoxide groups of 0.5–1 mole kg^{-1}. The sample (~ 0.05 g) of polypropene hydroperoxide, in a vacuum of 10^{-2} mmHg, was irradiated at 77°K in the cavity

of the radio-frequency spectrometer with filtered light from a DRSh-1000 mercury lamp. Formation of free radicals began immediately after the beginning of irradiation. The ESR signal is asymmetric ($g = 2.0047$, $\Delta H \simeq 60$ Oe) and consists of the ESR spectra of hydrocarbon radicals resulting from the isomerisation of alkoxy radicals superimposed on the spectra of peroxy radicals[102]. The rate of production of radicals, measured by the linear portion of the kinetic curve, is 4 times higher for irradiation with $\lambda < 300$ mμm than with $\lambda > 300$ mμm, and amounts to 6×10^{14} radicals min^{-1}. Thus, the hydroperoxide of atactic polypropene is decomposed at a significant rate not only by short-wave radiation but by longer-wave radiation as well. It is suggested that the high rate of decomposition of the hydroperoxide and of accumulation of radicals under the influence of light of $\lambda > 300$ mμm, i.e. in the region where the hydroperoxide absorbs very weakly, is due to the high quantum yield of this photoreaction.

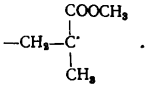
As has already been stated, free-radical concentrations during photoreactions in the liquid phase are minimal, and their detection lies at the very limit of performance of modern ESR radio-frequency spectrometers. However, ESR has been used with success[103-196] to study photoreactions in media which are very viscous at ordinary temperatures, as for example in the late stages of photopolymerisation. We shall discuss, as an illustration, the results obtained by Bresler and coworkers[106] in their ESR study of the photoinitiated polymerisation of methyl methacrylate (MMA), vinyl acetate (VA), and methacrylic acid (MAA). Photopolymerisation was induced both directly inside the cavity and externally, using PRK-4 lamps as the light source. When photopolymerisation was carried out outside the cavity of the radio-frequency spectrometer, the bulb containing the sample was placed in a quartz tube through which water from an ultrathermostat was circulated. Attempts to detect PMMA macroradicals in the early stages of photopolymerisation inside the cavity were unsuccessful because of the low sensitivity of the apparatus. Beyond about 50% conversion in the photopolymerisation of MMA and VA at 300°K, formation of a considerable number of macroradicals with a five-line ESR spectrum was observed (intensity ratio of the components 1 : 4 : 6 : 4 : 1, splitting 26 Oe). If the photoinitiation of the polymerisation is stopped at 60–80% conversion, the polymerisation effectively ceases. Most of the macroradicals under these conditions remain stable, and can undergo neither recombination nor monomer addition at room temperature. The ESR spectrum of the PMAA macroradicals is in no way different from the corresponding spectrum of the PMMA macroradicals. Since the polymer formed by the polymerisation of MAA is precipitated, the accumulation of macroradicals, captured by the gel being deposited, is not surprising[103,104]. The observed ESR spectra relate in the main to "captured" radicals, whose concentration is only indirectly related to the kinetics of the photopolymerisation process. The accumulation of "captured" radicals in homogeneous systems at relatively early stages of polymerisation stresses the inadequacy of the generally held views on the kinetics of the growth and disappearance of macroradicals. Evidently, a considerable proportion of the macroradicals is relatively stable because of the difficulty of access to the reactive centre deep within the tangle formed by the macromolecule. An important factor in this "capture" of macroradicals is whether the monomer is a good solvent or a poor solvent for the polymer. Hence, not all polymers "capture" macroradicals to the same extent. Furthermore, the higher the molecular weight, the more likely is the reactive centre to be screened by the polymer tangle. An attempt was made to study the fate of the radicals captured in PMMA after completion of the polymerisation: even at 330°K the ESR spectrum of a low-molecular-weight polymer changed quite rapidly, and the original five-component spectrum was replaced by a four-component spectrum with a 1 : 3 : 3 : 1 intensity ratio. This spectrum points to the appearance of a new radical in which the unpaired electron interacts not with four equivalent protons (as in the original radical) but with three. The rearrangement of the ESR spectrum is ascribed[106] to the ability of the macroradicals to capture a labile hydrogen atom at 330°K by the reaction



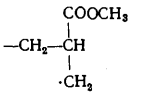
The ESR spectra in PMAA and PVA disappeared instantaneously on crossing the glass transition point.

However, the possibility must be considered that the initial ESR spectra were due to radicals formed by the photodecomposition of the resulting polymer rather than to radicals appearing during photopolymerisation.

Sorin and Tsaregradskii[107] have reported a study by ESR and optical spectroscopy of the photodegradation of PMMA at 77° and 300°K. By using molecular spectroscopy it was shown[108,109] that CO_2, CO, H_2, CH_3OH, methyl formate, etc. are produced when PMMA is irradiated with ultraviolet. It was also found that the photodegradation of PMMA is accompanied by a decrease in molecular weight, formation of monomer, and a decrease in strength. There is no doubt that photodegradation is accompanied by the appearance of intermediate free-radical products. In fact, irradiation of PMMA with the light of a DRSh-500 mercury lamp or with the filtered light (BS type filters) of a DKSSh-1000 xenon lamp produces free radicals whose ESR signal is the combination of a quintet and a quartet of lines of relative intensities 1 : 4 : 6 : 4 : 1 and 1 : 3 : 3 : 1 respectively. These radicals are stable and persist for several months. It has been shown that the first spectrum is produced by the radicals



For the second type of radical, the authors proposed the structure



arising from the first when the free valency on the carbon of the polymer chain captures a proton from the methyl group. It is found experimentally that the relative intensities of the quintet and the quartet are functions of the temperature and of the spectral composition of the active light: the intensity of the quartet decreases with rise in temperature and at 290°K only the quintet remains; the quartet is not formed when irradiation is with light of $\lambda \geq 340$ mμm, but it appears on subsequent irradiation with unfiltered light. Thus, the second (quartet) ESR signal could alternatively be assigned to the $\dot{C}H_3$ radical, formed in the primary act of short-wave ultraviolet irradiation.

4. Photodecomposition of Adsorbed Organic Compounds

The formation and stabilisation of active intermediate products on the surface is of enormous importance in heterogeneous catalysis. These intermediate products could be free radicals and ion-radicals. The first systematic study of adsorption by spectral methods is due to Terenin[110-113]. Under his direction, methods were developed for investigating adsorbed molecules and also the surface properties and the catalytic properties of adsorbents from visible, ultraviolet, and infrared absorption spectra. In recent years, the ESR method has been successfully applied to the study of the properties of adsorbed free radicals and of the nature of their interaction with the surface. In particular, the possibility of low-temperature stabilisation, on a silica gel surface, of active radicals such as atomic hydrogen and alkyl radicals has been demonstrated.

Kazanskii and coworkers[114,115] described a photochemical procedure for preparing and stabilising methyl radicals at 77°K from methyl iodide, adsorbed in a vacuum from the vapour onto the surface of silica gel. After irradiating this system for 4–6 h at 77°K with ultraviolet light (from a PRK-7 lamp), they observed the ESR spectrum of adsorbed methyl ($\dot{C}H_3$) radicals, consisting of four hyperfine structure components of half-width 1–2 Oe, splitting 23.3 Oe, and an unusual distribution of the intensity of the individual components (1 : 8.5 : 13 : 2.5 instead of 1 : 3 : 3 : 1). This is ascribed to the fact that adsorption of a methyl radical on the surface of silica gel causes the loss of two rotational degrees of freedom because of the coupling of the unpaired electron to the adsorbent. Only one axis of rotation remains, around the orbital of the unpaired p-electron. This rotation produces incomplete averaging of the anisotropic hyperfine and spin–orbital interaction, and therefore the ESR spectrum adopts an asymmetric form with a non-binomial distribution of component intensities[114]. The intensity of the signal does not alter on keeping the specimen for several hours at liquid nitrogen temperature. A decrease in intensity of the spectrum becomes noticeable 5 min after allowing the sample to warm up to −130°C. The spectrum has not completely disappeared after 30 min storage at −40°C. Hence it is evident that methyl radicals adsorbed on the surface of silica gel have a relatively high stability, well in excess of the stability of alkyl radicals in frozen solutions. These results show that quite active radicals prepared by photodecomposition of adsorbed compounds can be stabilised on the surface of solids. Furthermore, the results also show that the ESR method can give fairly detailed information on the geometry of the bond between adsorbed radicals and the surface, and on the type of motion of the radicals.

Tolkachev and coworkers[116] used the method (proposed by Kazanskii and Pariiskii) of photodecomposition of molecules adsorbed on a silica gel surface in order to stabilise and detect, at 77°K, benzyl radicals ($C_6H_5\dot{C}H_2$) produced by ultraviolet irradiation of benzyl chloride[98,104]. Theoretical calculations of the density distribution of the unpaired electron in the benzyl radical have been published[117,118]. The first experimental attempts at observing the hyperfine structure of the ESR spectrum of this radical in solid hydrocarbon glasses were unsuccessful[23]. In the more recent work[116] the benzyl chloride was adsorbed from the vapour phase, in a vacuum, on the surface of silica gel (of specific surface area 300 $m^2\ g^{-1}$) at room temperature, and was then irradiated with ultraviolet light from a PRK-7 high-pressure mercury lamp for 2–4 h at 77°K. The resulting ESR spectrum consisted of a triplet with a separation of 16.5 ± 1 Oe between the components. Each of the components was further split into a quadruplet with a constant spacing of 5.5 ± 0.5 Oe between its components. The triplet in this spectrum was due to the interaction between the unpaired electron and the protons of the $-\dot{C}H_2$ group. The low value of the splitting on the protons of the methylene group (16.5 instead of 23 Oe) suggests delocalisation of the unpaired electron into the π-system of the ring, and this is confirmed by the splitting of each component of the triplet into a quadruplet, due to interaction of the unpaired electron with three protons of equivalent hydrogen atoms of the ring. The agreement between experimental results and theoretical calculations is evidence that the spectrum was correctly interpreted. As in the previous case, no ESR spectrum could be obtained from the halogen atoms ($\dot{C}l$).

5. Photo-ejection of an Electron (Photoionisation)

Photoionisation is the extraction of an electron, under the influence of light, from a photoexcited molecule into a vacuum or into a medium, accompanied by free existence or capture of the photoemitted electron in the medium (trapping, solvation, etc.). Terenin[12] treats the photoionisation of organic molecules as a special case of the photodecomposition reaction: the photodissociation of the compound into oppositely charged ions (a molecular cation and an electron). However, the photoionisation reaction is often considered to be[119,120] the primary, elementary act of the oxidation–reduction process[121]. The term elementary photo-oxidation usually refers to the removal of an electron from a photoexcited molecule (the oxidisable component) to another molecule (the oxidising agent or electron acceptor), which has a positive electron affinity. The photo-oxidation of one compound is invariably accompanied by the reduction of another compound (the oxidiser). The mechanism and the energetics of the photoionisation and the elementary photo-oxidation process are quite different: this defines their individual roles and allows us to discuss the photo-extraction of an electron independently of oxidation–reduction photoreactions.

The removal of an electron under the influence of light (i.e. the photoelectric effect) has long been known for aromatic molecules in the solid state and in solution. The emission of an electron by light from organic molecules in the condensed phase was clearly demonstrated for the first time by Lewis and coworkers[119,120] by a spectroscopic investigation. It has also been known for a long time that the vapours of anthracene, diphenylmethane, aniline, diphenylamine, and α-naphthylamine show electrical conductivity under the influence of short ultraviolet light[122-124]. Terenin and Vilesov[125,126] have recently developed a powerful mass-spectrometric method of studying the photoionisation of vapours of aromatic compounds (including dyes) which enables the critical energy for the photoremoval of an electron in a vacuum to be determined with high precision.

Lewis and coworkers[119,120], and more recently Linschitz and coworkers[127], observed, in their spectroscopic investigations, coloured products from the interaction of near ultraviolet with frozen solutions at 90°K in EPA (a mixture of alcohol, isopentane, and ether in the ratio of 2 : 5 : 5 by volume) of various colourless aromatic compounds: amines, phenols, and the leuco-forms of dyes. The colouration of the solutions upon irradiation was caused by the photo-extraction of an electron from the colourless

aromatic compound with formation of a positively charged molecular radical-ion, for example

$$(C_6H_5)_3\dot{N} \xrightarrow{h\nu} (C_6H_5)_3\dot{N}^+ + e\,.$$

An analogous process occurs during the photo-extraction of an electron from aromatic compounds containing N, O, and S atoms, which have unshared electron pairs. The electron split off by the light remains trapped in the solid solution at 90°K. However, even a small temperature rise allows the medium to lose its rigidity and the trapped electron to recombine with the ion. Photoionisation of molecules can be induced also at ordinary temperatures by using a medium (such as boric acid glass, or polymers†) rigid enough to trap the photo-extracted electrons for an appreciable time. Since one of the products of the electron photo-extraction reaction is an unstable molecular ion with an unpaired electron and therefore paramagnetic, such a product can in principle be detected by the ESR method in the condensed phase.

Bijl and Rose-Innes[22] were among the first to apply the ESR method to the study of photo-processes in organic compounds, and in particular to the study of photoionisation. Their experimental materials were aromatic diamines, which are readily oxidised by light: tetramethyl-*p*-phenylenediamine (Wurster's base) and *p*-phenylenediamine. To stabilise the resulting radical-ions a, polymeric medium [poly(methyl methacrylate)] having a glassy state at ordinary temperatures was used instead of a low-temperature hydrocarbon glass. After 5 min irradiation with ultraviolet light from a high-pressure mercury lamp the film developed a brown and greyish-green colour accompanied by the appearance of an ESR signal consisting of a single line with $g = 2.001 \pm 0.002$. The paramagnetic product stabilised in this way survived for several months at room temperature. It is known[119] that the cation-radical of tetramethyl-*p*-phenylenediamine (Wurster's Blue) has absorption bands at 630, 580, 520, and 500 mμm, and therefore has a blue colour. Since the product obtained in these experiments is brown in colour, it may be assumed not to be the cation-radical of the diamine, but rather a free radical resulting from the interaction of that cation-radical with the medium.

Bennema and coworkers[130] made a detailed study of the formation of coloured photo-products by the ultraviolet irradiation of various aromatic hydrocarbons in boric acid glasses. Solid, glassy solutions of the following hydrocarbons in boric acid were irradiated: biphenyl, phenanthrene, terphenylene, tetracene, pyrene, perylene, and coronene. In every case the authors observed the formation of coloured products whose optical absorption and ESR spectra indicated the presence of singly charged, positive molecular ions of the corresponding hydrocarbons, produced by photoionisation. On heating the coloured glasses the colour disappeared, with simultaneous emission of the characteristic recombination phosphorescence of the particular hydrocarbon molecule.

Hoijtink and Zandstra[131] exposed to ultraviolet light methyltetrahydrofuran solutions of the negative ions of aromatic hydrocarbons in a vacuum at 77°K, and obtained spectroscopic evidence of their photoionisation:

$$M^{2-} \xrightarrow{h\nu} M^- + e;\ M^- \xrightarrow{h\nu} M + e\,.$$

† Electron photo-extraction has recently been observed in the flash-irradiation of a liquid solution of triphenylamine in hexane[128] and of diphenylamine and triphenylamine in electron-acceptor solvents like CCl_4, $CHCl_3$, and CH_2Cl_2 at 300°K,[129] by the appearance of a short-lived (10^{-4} s) optical absorption spectrum due to the corresponding radical cation.

In the first experiments, no evidence could be found of capture of the ejected electrons by the alkali metal cation (Na^+) or by the solvent matrix. However, on repeating the experiments including ESR, visible, and infrared spectroscopy of the irradiated solutions, van Voorst and Hoijtink[132] obtained clear proof of the capture of the ejected electrons in the holes of the network of the frozen matrix. As in the earlier experiments, negative ions were obtained by treating a 3-methyltetrahydrofuran solution of the appropriate aromatic hydrocarbon (tetracene, perylene, pyrene) with an alkali metal in a vacuum:

$$M + X \rightarrow M^- + X^+;\ M^- + X \rightarrow M^{2-} + X^+;\ (X = \text{Li, Na, K})\,.$$

After irradiation at 77°K, with light corresponding to their absorption bands, the optical absorption spectra of the frozen solutions of singly and doubly charged ions of the solution changed to those of uncharged and singly charged ions respectively. At the same time, an absorption band ($\epsilon = 3-4 \times 10^4$) appeared in the infrared region at 1300 mμm, accompanied by a singlet ESR line with $g = 2.002$ and $\Delta H = 4.5$ Oe, increasing with duration of exposure to the photoionisation process. On thawing the glassy solution, or under the influence of visible light ($330 < \lambda < 600$ mμm), the infrared band disappears, and the initial spectra of the negative ions are re-established. These results imply that the phototransfer of an electron is a reversible process in a solid solution. The minimum quantum energy (2 eV) needed to inhibit the infrared band can be identified with the depth of the trap in which the ejected electron is captured. Since both the shape and the position of the infrared band and of the ESR signal are independent of the nature of the aromatic hydrocarbon and of the alkali metal ion, the author concludes that these signals are due to unpaired electrons trapped in holes of the matrix at 77°K.

The photoionisation of aminoacids and proteins at low temperatures was first investigated by the ESR method by Allen and Ingram[133], who attempted to obtain unpaired electrons by ultraviolet irradiation ($\lambda = 365$, 254 mμm) of four amino-acids (tyrosine, methionine, cystine, and leucine) and four proteins (insulin, insulin with protamine, ox albumen, and egg albumen). All preparations were examined as aqueous solutions or suspensions at 96°K. The experimental results obtained led the authors to the conclusion that radicals are formed by ultraviolet irradiation of proteins and amino-acids, photoionisation of the starting compounds being involved in the primary process. Relatively little has been published on free-radical states in amino-acids and proteins. The first papers on this topic by Grossweiner[134,135] appeared after the development of the techniques of flash photolysis and fast spectroscopy, which allow short-lived radical-ion intermediates to be studied in solutions of aromatic hydrocarbons. Studies of low-temperature thermoluminescence in ultraviolet-irradiated aqueous solutions of aromatic amino-acids and proteins allowed to warm up from 77° to 110°K led Vladimirov and Roshchupkin[136] to ascribe the effect to the recombination of two intermediate products of the first step of the photochemical reaction.

By using the ESR method to study the primary photochemical processes in amino-acids and proteins, Azizova[137-140] was able to investigate the paramagnetic species resulting from ultraviolet irradiation and to give a convincing account of the photoionisation of the biologically important compounds being examined. Ultraviolet irradiation of aromatic amino-acids in the crystalline state at 77°K produces a singlet ESR signal with a *g*-factor close to the free-electron value and $\Delta H = 16$ Oe (tyrosine, tryptophan) or 20 Oe (phenylalanine). A singlet ESR

signal with $\Delta H = 13$ Oe appears in ultraviolet-irradiated glycyltyrosine and glycyltryptophan. Subsequent irradiation of the amino-acids with light of $\lambda = 320-700$ mμm, or a rise in temperature to 300°K of the ultraviolet-irradiated sample, produces a 1.5–2-fold decrease in the intensity of the singlet ESR signal. Irradiation with ultraviolet light of aqueous solutions of aromatic amino-acids (tryptophan, tyrosine) at 77°K causes photoionisation, accompanied by the appearance of positive radical-ions of the amino-acids and of electrons trapped in the medium. The evidence for this is a singlet ESR signal with $\Delta H = 20$ Oe and a g-factor close to the free-electron value, which is suppressed by light of $\lambda = 320-700$ mμm or by heating the sample. The paramagnetic centres which absorb light in this region and disappear on heating are hydrated electrons. Ultraviolet irradiation of water solutions of proteins at 77°K also causes photoionisation of the aromatic amino-acid residues and decomposition of the sulphur-containing amino-acid residues. Hélène and coworkers[141] observed, in aqueous solutions of purine, adenosine, and guanosine at 77°K, the formation under ultraviolet irradiation of a singlet ESR signal by the photoreaction

$$Pu \xrightarrow{h\nu} Pu^{+} + e$$

The singlet ESR signal consists, strictly, of a signal from the Pu^{+} radical-cation and a signal from the hydrated electron. The latter can be set free from the "traps" in the ice lattice under the influence of visible light of $\lambda < 450$ mμm, and this is manifest (as in the previous work of Azizova and coworkers) by a decrease in the amplitude of the ESR signal. The electrons set free by the light can be captured by Pu^{+} ions or by neutral Pu molecules, which have a high electron affinity[142]. A theoretical calculation of the ionisation energy of π-electrons gives a value of the order of 8 eV for nucleic acid bases[143]. The energy quantum of the active photon ($\lambda = 254$ mμm) corresponds to 5 eV and cannot produce photoionisation of these molecules. The energy of the triplet state in purine, adenosine, and guanosine is close to 3.4 eV. Assuming a two-photon mechanism for the photoionisation of nucleic acid bases, as suggested by the authors[141], an ionisation potential of the order of 8 eV can be attained by the absorption of the second photon ($\lambda = 254$ mμm) by the triplet molecule of the base (3.4 + 5 = 8.4 eV).

The possibility of a two-quantum process of this kind for the ionisation of aromatic compounds in solid solutions at 77°K was first proposed in 1963 by Terenin and the present writer[144,145]. Since then, the two-photon mechanism of the photoionisation of aromatic compounds has been convincingly demonstrated in a number of instances[146-154].

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The purpose of this review has been to give a systematic and ordered account of the very numerous photochemical investigations in which the ESR method has been used to throw light on the paths followed by photodecomposition reactions. Most of the photochemical processes had been previously investigated spectrophotometrically. The EST method, on the other hand, had been used mainly to confirm various photodissociation mechanisms. In a number of instances the ESR method has given new and original results. It must be stressed, however, that the successful application of the ESR method in photochemical investigations requires a sound knowledge of the spectral properties of photochemically active systems, a keen appreciation of possible photoprocesses in these media, including secondary processes, and skilful experimentation (choice of medium, temperature, light source, etc.). The ESR method will become a powerful physical method of investigation only if used in conjunction with other methods, and in particular with optical spectroscopy and mass-spectroscopic analysis.

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Application of the Ferromagnetic Resonance Method in the Study of Heterogeneous Catalysts

A.A.Slinkin

The main features of the ferromagnetic resonance method are discussed in the context of the study of heterogeneous catalysts. Results obtained by this method are examined, and possible future developments are pointed out.

CONTENTS

I. Introduction 643
II. The ferromagnetic resonance method 643
III. Experimental work on the application of the ferromagnetic resonance method to the study of catalysts 649

I. INTRODUCTION

A detailed knowledge of the physical properties and structure of real catalysts is one of the prerequisites for the development of a theory of heterogeneous catalysis able to pave the way to the synthesis of catalysts of prescribed chemical composition and structure, leading to the development of new chemical processes and to the improvement of existing ones. Unfortunately, and in spite of the large number of catalysts used in industry and in laboratories, this information is lacking in most cases. Only during the last 10–15 years, as a result of the application of various physical methods, has some progress been possible in this direction. The study of a real, multicomponent heterogeneous catalyst by physical methods is a very complex problem. A catalyst of this type contains a very large number of defects, frequently of unknown nature. In these circumstances, quantitative interpretation of the results of physical measurements becomes very difficult, and quantitative calculations are ambiguous. The position is made worse by the change in both the number and the nature of the defects induced by the catalytic reaction itself. A study of these systems would be meaningless to a solid-state physicist concerned with studies at the single-crystal level. Yet, we are forced to work with these materials if we wish to inquire into the nature of heterogeneous catalysis.

At the moment, the only way out of the dilemma is to examine a given catalyst by the greatest possible number of physical methods which, by cross-checking and complementing each other, can offer a fuller understanding of the real physical structure of heterogeneous catalysts. Therefore, the use of any physical method which can reveal new facets in the study of catalyst structure is highly desirable. Accordingly, this review will deal with the ferromagnetic resonance method and its application to the study of various nickel catalysts.

II. THE FERROMAGNETIC RESONANCE METHOD

1. General Remarks

Static magnetic methods have been applied for a number of years to the study of catalysts [1-5], with valuable results for both paramagnetic and ferromagnetic catalysts. The application of static magnetic methods (i.e. the measurement of magnetic properties in constant fields) to the analysis of the structure and valency characteristics of paramagnetic ions depends essentially on the use of the Langevin equation and Curie's law.

In paramagnetic materials the magnetic moments of the ions, atoms, or molecules are pointing in all directions in space with equal probability, and the total magnetic moment is zero. When such a material is placed in a magnetic field the magnetic moments become oriented along the field, and the number of moments oriented with the field becomes greater than the number oriented against the field. As a result, the material becomes magnetised, and we observe a positive magnetic susceptibility.

Noting that the magnetic moments in a paramagnetic material immersed in a magnetic field of intensity H are experiencing simultaneously the randomising effect of thermal motion and the orienting effects of the field, Langevin obtained a formula relating the magnetisation to the field strength (H) and to the absolute temperature (T):

$$\sigma = \sigma_0 \left[\coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \right], \qquad (1)$$

where σ is the magnetisation per unit weight of the material, σ_0 the limiting magnetisation per unit weight (saturation magnetisation), μ the magnetic moment of the ion, atom, or molecule, H the field strength in Oersteds, k Boltzmann's constant, and T the absolute temperature.

Fig. 1 shows the variation of the Langevin function with the value of the parameter $\mu H/kT$. It is obvious that the function tends to saturate at high values of H (i.e. tends to the value σ_0). However, with paramagnetic materials fields in excess of 10^6 Oe, which are inaccessible in practice, are needed to reach the saturation region, i.e. to obtain values of $\mu H/kT > 1$. The only way to obtain a Langevin curve covering a significant range of the parameter $\mu H/kT$ with paramagnetic materials is to work at low temperatures and relatively high field strengths. Thus, at $T \simeq 1°K$ and $H \simeq 10^4$ Oe, $\mu H/kT \simeq 1$. More commonly, at room temperature and fields of the order of 10^3 Oe, the value is

$$\mu H/kT = \frac{0.93 \cdot 10^{-20} \cdot 10^4}{1.38 \cdot 10^{-16} \cdot 300} \simeq 0.02, \text{ i.e. } \mu H \ll kT.$$

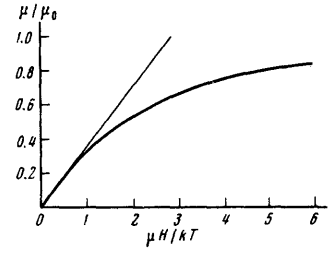

Figure 1. Dependence of the relative magnetic moment μ/μ_0 upon the parameter $\mu H/kT$.

In this case we can expand the Langevin function into a series for small values of the parameter $\mu H/kT$, and retain only the first term of the expansion, giving

$$\sigma = \sigma_0 \frac{\mu H}{3kT} \qquad (2)$$

which is the tangent to the curve of Fig. 1, or

$$\sigma = N\mu \frac{\mu H}{3kT},$$

where N is the number of magnetic particles of magnetic moment μ in 1 g of the material.

$$\chi = \frac{\sigma}{H} = \frac{N\mu^2}{3kT} \quad \text{or} \quad \chi T = C \qquad (3)$$

is Curie's law, where χ is the magnetic susceptibility.

Thus, we obtain Curie's law, where the Curie constant $C = \frac{N\mu^2}{3k}$. However, it must be stressed that Langevin obtained his formula on the assumption that: 1) we are dealing with a gas of paramagnetic particles, and 2) the magnetic moments of the particles are not mutually interacting. In practice, however, plots of $\frac{1}{\chi}$ against T do not pass through the origin as required by formula (3), and χ is found to vary with temperature by the more complicated law

$$\chi = \frac{C}{T - \Delta} \qquad (4)$$

(the Curie–Weiss law), where Δ can be either positive or negative.

This deviation from Curie's law arises from the interaction of the magnetic moments of neighbouring particles, and the constant Δ (Weiss's constant) characterises the magnitude of this interaction in the simplest cases. Nevertheless, the forces between neighbouring ions, atoms, or molecules in paramagnetic materials are not very large, and their magnetic susceptibilities are negligible.

In addition to the static magnetic methods of investigating paramagnetic catalysts, the methods of microwave spectroscopy have come to the fore in recent years, and in particular the electron paramagnetic or electron spin resonance (ESR) method. Details of the method and of the results obtained in studies of heterogeneous catalysts have been discussed elsewhere[6,7]. The resonance conditions for the ESR method are given in the form

$$h\nu = g\mu_B H_0$$

where h is Planck's constant, ν the frequency of the radiation absorbed, g the spectroscopic splitting factor, μ_B is the Bohr magneton, and H_0 the external magnetic field.

We can recast this formula in terms of angular Bohr frequencies:

$$h\nu = \hbar\omega_{res} = g\mu_B H_0, \text{ or}$$
$$\omega_{res} = \gamma H_0, \qquad (5)$$

where

$$\omega_{res} = 2\pi\nu; \quad \gamma = \frac{g\mu_B}{\hbar}, \text{ and } \hbar = \frac{h}{2\pi}.$$

In general, and like the static magnetic susceptibility method, the ESR method when applied to the study of paramagnetic materials relates to the spin and orbital moments of isolated particles (for example, highly dilute solid solutions of paramagnetic ions in a diamagnetic matrix), or alternatively to the relatively weak interactions of the magnetic moments of neighbouring particles.

A situation different in principle is observed in studies of resonance phenomena in ferromagnetics[8]. Because of the very strong exchange interaction between atoms in a ferromagnetic crystal, the magnetic moments of neighbouring atoms are oriented parallel to each other even in the absence of a field, and the application of a field produces gigantic values of the magnetisation (10^4–10^5 times higher than in paramagnetics). The magnetisation process will be considered in more detail in the following sections. The existence of strong exchange interactions, and various other effects, in ferromagnetic substances makes the interpretation of ferromagnetic resonance spectra in polydisperse systems much harder than the interpretation of ESR spectra. Thus, formula (5) must be written, for the case of ferromagnetic resonance, in the form

$$\omega_{res} = \gamma H_{eff}, \qquad (6)$$

where $H_{eff} = H_0 + H'$, and H' is some additional field whose value depends on the nature of the specimen, the experimental conditions, the shape of the particles, the presence of defects, and so on. Failure to allow for this additional field can lead to serious errors, particularly in the determination of the g-factor.

We shall now discuss the main factors which determine the resonance conditions in ferromagnetics, and on the basis of this analysis we shall review the work on the study of catalysts by this method.

2. Influence of Crystallographic Magnetic Anisotropy on the Resonance Frequency and on ΔH

The *magnetic crystallographic anisotropy* effect is one of the most important factors which determine the resonance frequency, and the line width (ΔH) of ferromagnetic resonance, in studies of polydisperse systems. Basically, the nature of the effect is as follows. Let us consider the magnetisation of single crystals of Ni, Fe, and Co as a function of the applied external field and its orientation with respect to the crystal axes. As Fig. 2 shows, an axis along which the crystal can most easily be magnetised exists in these crystals (as also in other ferromagnetics). For example, for Ni this axis is the [111] axis or body diagonal of the cube. The major planes of a cubic crystal and the directions of the corresponding axes are shown in Fig. 3.

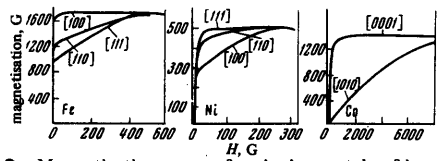

Figure 2. Magnetisation curves for single crystals of iron, nickel, and cobalt.

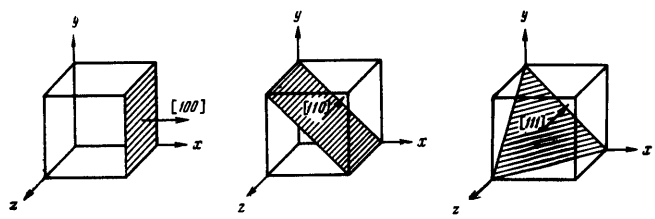

Figure 3. Main crystal planes and axes in a cubic crystal.

How does magnetisation of a magnetically anisotropic crystal occur? If the external magnetic field is parallel to the easy magnetisation axis, the crystal is magnetised practically to saturation in very small fields. If, on the other hand, the direction of magnetisation by the external field is at a definite angle to the easy magnetisation axis, a greater expenditure of energy is required to magnetise the crystal to saturation, and therefore saturation is reached at higher magnetic fields. The physical explanation of the existence of magnetic anisotropy depends on spin–orbital interactions in the crystal. An atom (or ion) in the crystal experiences crystal fields having a definite symmetry, which lead to the removal of orbital degeneracy and therefore to an anisotropic distribution of orbital magnetic moments. The spin magnetic moments (which are mainly responsible for ferromagnetism) are affected by this anisotropic distribution through spin–orbital coupling.

The magnetic anisotropy energy is expressed by the magnetic anisotropy constants, which are strongly temperature dependent. Fig. 4 shows the temperature variation of the first magnetic anisotropy constants (K_1) of Ni, Fe, and Co. It can be seen that the magnetic anisotropy constant is greatest for Co, and that the constants for Ni and Fe are relatively lower. The most striking feature of the temperature dependence of K_1 for nickel is a rapid decrease with increase of temperature, the constant K_1 almost vanishing at 100°. [Unless stated otherwise, all temperatures are in °C (Ed. of Translation).]

How are the conditions for ferromagnetic resonance affected by these peculiarities of the magnetisation of ferromagnetic crystals? It is obvious that if the magnetic

field H_0 is applied in the direction of the axis of easy magnetisation the anisotropy energy will be a minimum. For the case of an Ni single crystal, in which $K_1 < 0$, it has been shown[9] that when $\Theta = 0°$ (difficult magnetisation axis, [100]) we have

$$\frac{\omega_{res}}{\gamma} = H_0 - \frac{2(K_1)}{\sigma_0}, \qquad (7)$$

where σ_0 is the saturation magnetisation and K_1 is the anisotropy constant.

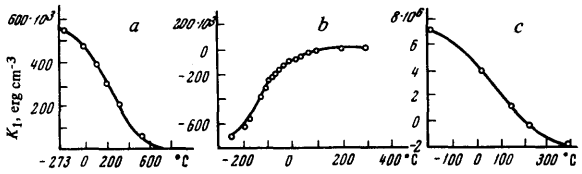

Figure 4. Temperature dependence of the first anisotropy constant (K_1):
a) Fe; *b*) Ni; *c*) Co.

When $\Theta = 54°44'$ (easy magnetisation axis, [111])

$$\frac{\omega_{res}}{\gamma} = H_0 + \frac{4}{3}\frac{(K_1)}{\sigma_0}, \qquad (8)$$

In these formulae the constant external field H_0 together with the additional field resulting from anisotropy,

$$2\frac{(K_1)}{\sigma_0} \quad \text{or} \quad \frac{4}{3}\frac{(K_1)}{\sigma_0},$$

constitute the effective field H_{eff} used in formula (6). Thus, with single crystals it is possible to find H_{eff} and to calculate ω_{res} by experimentally varying the angle between the direction of H_0 and the crystal axes.

In studies of real catalysts we are not dealing with single crystals. One commonly deals with Ni microcrystals in a diamagnetic or paramagnetic matrix ($Ni-Al_2O_3$, $Ni-SiO_2$, $Ni-Cr_2O_3$, etc.) or with highly disperse nickel powders (Raney nickel). In these systems the Ni crystallites have arbitrary orientations of the easy magnetisation axis with respect to the direction of the external field H_0, resulting in a range of resonance fields (at a fixed value of ω) for the various Ni crystallites. This causes significant line broadening, and often produces asymmetry in the shape of the line and a shift of the g-factor. This is one of the forms which non-uniform magnetisation of the sample can take.

Obviously, if $K_1 = 0$ and no other sources of non-uniform magnetisation are present, it follows from formulae (7) and (8) that $H_{eff} = H_0$, and formula (5) can be applied. From this formula, which is characteristic for paramagnetic resonance, the g-factor can be accurately calculated. Hence, the only way of avoiding the magnetic anisotropy effect in studies of polydisperse catalysts is to measure the ferromagnetic resonance at high temperatures, when $K_1 \simeq 0$ and the g-factor can be calculated by formula (5).

3. Influence of Shape Anisotropy on the Resonance Frequency and ΔH

In addition to the non-uniformity of magnetisation due to magnetic crystallographic anisotropy, the true internal magnetic field H_{eff} in a ferromagnetic sample differs from the external magnetic field H_0 through the influence of the geometrical shape of the sample. The physical basis of this effect can be explained as follows. If a sample having a high magnetisation is placed in the uniform external field H_0, magnetic charges giving rise to a formal magnetic field H_e in opposition to the external field H_0 are generated on the surface of the specimen (Fig. 5). This field, called the demagnetising field, is proportional to the magnetisation of the specimen:

$$H_e = -N\sigma_0, \qquad (9)$$

where N is the demagnetisation factor.

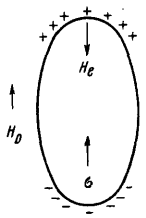

Figure 5. Formation of the demagnetising field H_e.

Hence, the field experienced by the specimen is not H_0 but a field H_{eff} given by

$$H_{eff} = H_0 - N\sigma_0 = H_0 - N\chi H,$$

whence

$$H_{eff} = \frac{1}{1+\chi N} H_0.$$

Since ferromagnetics have very high χ values, the field H_{eff} can differ very substantially from H_0. Strictly speaking, formula (9) is applicable only to ellipsoidal specimens of other shapes. The factor N in formula (9) is the total demagnetisation factor, but it is more convenient to consider factors of the form N_x, N_y, and N_z along the principal semi-axes of the ellipsoid l_x, l_y, and l_z. The relationship between N_x, N_y, and N_z is

$$N_x + N_y + N_z = 4\pi.$$

Allowing for the demagnetising effect of the surface, Kittell obtained the following formula for the resonance frequency

$$\frac{\omega_{res}}{\gamma} = \sqrt{[H_0 + (N_x - N_z)\sigma_0][H_0 + (N_y - N_z)\sigma_0]} \qquad (10)$$

showing that the resonance condition depends on the shape of the specimen and on σ_0. Thus, if we are considering a specimen whose shape is an ellipsoid of revolution about the z-axis ($l_x = l_y = l_\perp$; $l_z = l_\parallel$), it follows that $N_x = N_y = N_\perp$ and $N_z = N_\parallel$, so that formula (10) becomes

$$\omega_{res} = \gamma(H_0 - \sigma_0 \Delta N), \quad \text{and} \quad \Delta N = N_\parallel - N_\perp.$$

A graphical expression for the dependence of the shape anisotropy factor ΔN on the ratio of the longitudinal to the radial axes of the ellipsoid $\left(n = \frac{l_\parallel}{l_\perp}\right)$ can be obtained[9] (see Fig. 6).

If follows from the graph that only in the case of a sphere ($n = 1$) does the effect of shape anisotropy on the resonance condition vanish, leading to formula (5), i.e.

$$\omega_{res} = \gamma H_0.$$

The shape of the sample has a very substantial effect on the value of the applied field corresponding to resonance. Thus, for iron (with $\sigma_0 = 1700$ G), the following resonance fields have been observed[9] using specimens of different shape (frequency 10^4 MHz, $\lambda \simeq 3$ cm).

Sphere	$H_{res} \simeq 3570$ Oe
Disk∥	$H_{res} \simeq 530$ Oe
Cylinder⊥	$H_{res} \simeq 12500$ Oe
Disk⊥	$H_{res} \simeq 26800$ Oe.

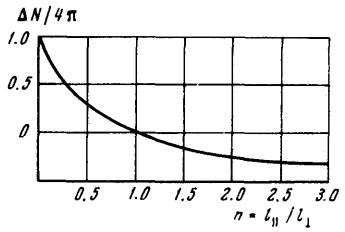

Figure 6. Variation of the difference between the longitudinal and the radial demagnetisation factor of an ellipsoid of revolution with the ratio of the half-axes.

Since a catalyst may contain particles of widely different shape, line broadening can occur through the increased range of resonance fields. However, unlike the broadening caused by magnetic crystallographic anisotropy, this type of broadening should be relatively insensitive to the measurement temperature, since the distribution of particle shapes during measurements of the temperature dependence of line width should remain essentially constant (provided that sintering is not taking place). Extremely interesting in this context is an attempt[10] to investigate the shape of ferromagnetic cobalt particles from the shape of the line. The ferromagnetic resonance of a polycrystalline Co–Cu alloy containing 2% of Co was measured as a function of aging at high temperatures. The calculated shapes of the resonance curve for disordered assemblies of plates, spheres, and rods are shown in Fig. 7*a*. Inspection of the shape of the resonance curves with increasing time and temperature of heat treatment (Fig. 7, *b*–*d*) shows that the particles are almost spherical in the original alloy, but they become larger and plate-like during aging. Thus, the shape of the ferromagnetic particle can be inferred from the features of the resonance curve if due allowance is made for all the other factors which influence the trend of the curve.

4. Domain Structure, Superparamagnetism, and Relaxation Processes

We have already noted the presence in ferromagnetics of strong exchange interactions as a result of which the magnetic moments of the atoms take up parallel directions. We shall now examine in greater detail the magnetisation of ferromagnetic substances. Generally speaking, a ferromagnetic could be expected to be fully magnetised at temperatures below the Curie point even in the absence of a field. Such, however, is not the case, and the modern theory of ferromagnetism offers the following explanation. Consider a ferromagnetic single crystal which has become spontaneously magnetised to saturation in the absence of an external field (Fig. 8*a*). This crystallite can be treated as a permanent magnet, giving rise to a surrounding magnetic field containing an appreciable amount of magnetic energy. However, any system must tend towards a state of minimum free energy. Can this happen in our case? Evidently, if the ferromagnetic crystallite is broken into a number of regions such that the total magnetisation in each pair of neighbouring regions points in opposite directions, the volume occupied by the external magnetic field and the energy of the field will decrease as the number of these regions increases (Figs. 8*b* and 8*c*). A region having only one direction of magnetisation, i.e. a region magnetised to saturation, is called a *domain*. This type of domain structure in ferromagnetic materials results in the magnetic moments at the boundaries between neighbouring domains being oriented in different directions. However, a state in which the magnetic moments are oriented in the same direction is energetically favourable in ferromagnetics. Therefore, energy must be expended to produce opposing orientations of the magnetic moments in the boundary region between domains. This energy is termed the *energy of the domain wall* †. Thus, the fragmentation of a ferromagnetic crystallite into domains involves both a decrease in the energy of the magnetic field outside the crystal and an expenditure of energy in the formation of domain walls. Hence, domain formation will continue until the energy required to form an additional domain becomes equal to the decrease in energy of the magnetic field outside the crystal.

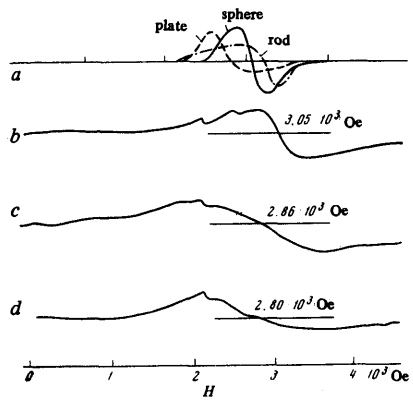

Figure 7. Theoretical and experimental ferromagnetic resonance lines for a Co–Cu (2% Co) alloy[10];
a) theoretical shape of the curve for particles of various shapes;
b) 30 min aging at 600°, average size of Co particles 25 Å;
c) 15 h aging at 600°, average size of Co particles 65 Å;
d) 20 min aging at 800°, average size of Co particles 300 Å.

Fig. 9 is a schematic representation of the magnetisation of a ferromagnetic crystal including its domain structure. In a real crystal the magnetisations of adjacent domains are oppositely oriented, and the total magnetisation is zero (Fig. 9*a*). Upon the application of an external magnetic field, the domains which happen to be magnetised in the

† The inversion of the direction of the magnetic moment at the boundary between domains does not occur abruptly, i.e. within the limits of one atomic layer, but gradually, and it involves hundreds of atomic layers. Therefore the thickness of the boundary wall can be as large as several hundred Ångstroms.

direction of the external field grow at the expense of other domains with a less favourably oriented magnetisation, leading to a movement of the domain walls (Fig. 9*b*). This process is accompanied by an increase in magnetisation. In small magnetic fields the displacement of the domain walls is reversible, and the magnetisation returns to zero when the field is removed. A much more complex situation obtains when large magnetic fields are used. Real crystals invariably contain defects, dislocations, impurities, etc. When a moving domain wall meets one of these defects its progress becomes uneven, discontinuous, and accompanied by a loss of magnetisation energy. As a result, this part of the curve becomes irreversible. Lastly, in large fields, when some domains have already grown at the expense of others and the magnetisation of the former is directed along the field, there are some residual domains whose magnetisation does not coincide with the direction of the applied field (Fig. 9*c*). Larger fields are needed to coerce the magnetic moments of these domains into the direction of the external magnetic field. The overall magnetisation curve is shown in Fig. 10.

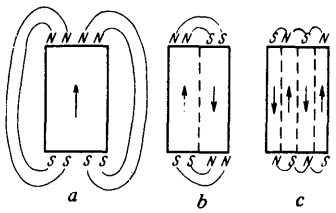

Figure 8. Formation of a domain structure.

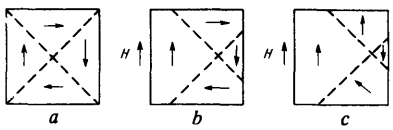

Figure 9. Magnetisation of a ferromagnetic with participation of the domain structure.

So far we have been concerned with a single crystal of a ferromagnetic material subdivided into domains. Real ferromagnetic materials are not usually monocrystalline (particularly in the case of ferromagnetic catalysts), but rather an assembly of a large number of crystallites of various sizes. According to its size, each crystallite is divided into a larger or smaller number of domains. The structure of a real ferromagnetic of this type is shown in Fig. 11. It is evident that its magnetisation can be treated in the same way as that of a single crystal, as was done above.

The domain structure of the specimen can influence the character of the ferromagnetic resonance[9]. In all the formulae given above it has been assumed that the specimen is magnetised to saturation, i.e. consits of a *single* ferromagnetic region of arbitrary magnetisation. Indeed, in the majority of ferromagnetic resonance experiments (including studies on catalysts) this condition is satisfied, because very high magnetic fields are used (several thousand Oersted). Allowance for the domain structure is essential in work with weak fields, when saturation magnetisation may not be achieved, leading to non-uniformity of magnetisation and therefore to line broadening and to a shift in the g-factor.

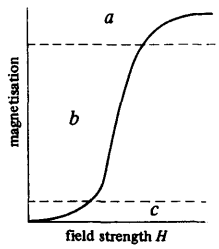

Figure 10. Characteristic magnetisation curve of a ferromagnetic: *a*) rotation processes; *b*) irreversible motion of domain walls; *c*) reversible motion of domain walls.

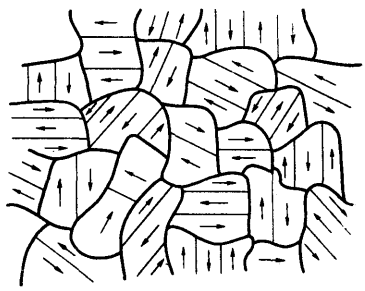

Figure 11. Microstructure of a non-magnetised polycrystalline ferromagnetic.

Let us consider the effect on the magnetic properties of the particles of size significantly less than the domain size. A one-domain particle, like a single crystal, has an axis of easy magnetisation, and the total magnetic moment of the particle in the absence of a field is oriented along the axis of easy magnetisation. Because of the large exchange interactions, the magnetic moments of neighbouring atoms have parallel orientations, and thermal motion cannot destroy the orientation of the resulting magnetic moment in the domain. When the size of the magnetic particles is drastically reduced the situation can be reached when $kT > K_1V$, where K_1 is the anisotropy constant and V is the volume of the particle. In this case the total magnetic moment of the particle will respond to thermal fluctuations, which will be opposed by the external magnetic field. Thus, the behaviour of the total magnetic moment of a small ferromagnetic particle is not unlike that of paramagnetic ions or molecules. Therefore, the temperature dependence of the magnetisation of these particles can be formally described by the Langevin equation (1), with the only difference that in Eqn. (1) μ is the magnetic moment of the paramagnetic ion, atom, or molecule, whereas in the present case μ is the magnetic moment of the particle, equal to $\mu_i n$ where μ_i is the magnetic moment at saturation of the ferromagnetic (0.6 μ_B for Ni) and n is the number of atoms in the particle. In contrast to classical paramagnetic

particles, the magnetic moment of these very small ferromagnetic crystals is thousands of times greater, and therefore Bean[10,11] has proposed the term "superparamagnetism" for this effect in ferromagnetics.

Since the magnetisation of these particles is formally described by the Langevin equation, the size of the particles can be calculated from the results of magnetic measurements. If the thermal energy is much greater than the energy of the interaction between the magnetic moment and the field, i.e. $kT \gg \mu H$, we have

$$\frac{\sigma}{\sigma_0} = \frac{\mu_{Ni} n H}{3kT}.$$

This equation is fully identical to Eqn. (2). If σ/σ_0 and H are known, we can determine $\mu_{Ni}n$, whence n, and therefore also the particle size, can be calculated.

The problem of the particle size determination of finely divided ferromagnetics, and the thermodynamic study of their magnetic properties, have already been discussed in detail[4,5]. We shall briefly consider these questions to arrive at a better understanding of ferromagnetic resonance in systems of small ferromagnetic particles.

Exchange forces, leading to narrower resonance lines, and dipole–dipole (magnetic) forces, leading to line broadening, are present in both paramagnetic and ferromagnetic substances. However, exchange interaction is very much stronger in ferromagnetics than in paramagnetics[12], and therefore quite narrow resonance lines (400–600 Oe) can be obtained with fairly coarse ferromagnetic particles. For iron single crystals lines as narrow as 40–60 Oe are possible. The situation is quite different with "superparamagnetic" particles of 10–15 Å dimensions. As stated above, thermal motion in these particles imposes a fluctuation on the total magnetic moment, the magnetisation of the particles is greatly reduced, and the Curie point is abnormally low[5,13]. All these phenomena arise from the decreased exchange interaction in particles of this type. As a result, resonance lines can become extremely broad and practically undectable (due to dipole–dipole broadening) in catalysts with a low content of ferromagnetic supported on a carrier of large surface area (Ni–SiO_2, Ni–Al_2O_3, etc.) and therefore consisting of small particles. In these cases the ferromagnetic resonance signal can be developed by sintering the catalyst, which increases the particle size of the ferromagnetic.

However, the dependence of the width of the resonance line on the disperseness of the ferromagnetic is a complex problem, and relevant data in the area of catalyst studies are practically non-existent. Some work in this general area has been done on ferromagnetic resonance in thin layers[14]. Fig. 12 shows the effect of the thickness of a Co film on the width of the ferromagnetic resonance line. The steep rise of ΔH at film thicknesses below 500 Å is ascribed to structural non-uniformity of the thin layers, implying non-uniformity of magnetisation and consequent line broadening. However, the results of studies of ferromagnetic resonance in thin layers (Ni, Co, Fe) cannot be directly applied to catalysts of the ferromagnetic metal–carrier type.

There is yet another effect tending to produce non-uniform magnetisation and a broadening of the absorption line in work with metallic ferromagnetics: the so-called "skin effect". This effect arises from the finite (1000–10 000 Å) depth of penetration of a high-frequency field in metals, resulting in non-uniform magnetisation in depth of the crystal. In studies of catalysts this effect can be ignored in most cases, because ferromagnetic crystals on a carrier are usually much smaller than the range of thicknesses quoted above.

The temperature dependence of the width of the ferromagnetic resonance line in ferromagnetic metals is also very interesting. For these materials (and in particular for Ni) ΔH remains practically constant between room temperature and the temperature of liquid helium, and increases steeply on approaching the Curie point[15] (Fig. 13).

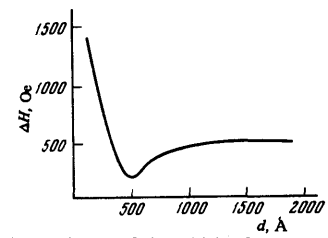

Figure 12. Dependence of the width of the resonance curve on the thickness of thin films of Co.

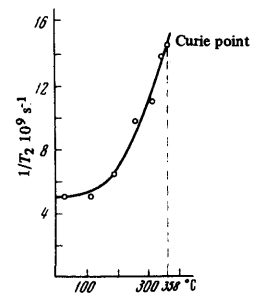

Figure 13. Dependence of relaxation frequency $1/T_2$ (proportional to the line width) on temperature, for Ni.

In this section we have considered various factors which influence the width of the ferromagnetic resonance line and the g-factor. If it were possible to exclude all the effects tending to broaden the distort the absorption curve, one could arrive at the true line width determined only by the relaxation processes in the ferromagnetic. The characterisation of the relaxation processes actually responsible for the width of the true absorption line is a complicated problem which has not yet been fully resolved[16]. An important consideration is the fact that electron–spin relaxation through the conduction electrons in a metal may be the most important of the various relaxation processes available to ferromagnetic metals and capable of giving rise to a resonance line of finite width. If such is the case, it should be possible to change the ferromagnetic resonance conditions and thus attempt to explain, for example, the interaction between metal and carrier, by somehow changing the concentration of conduction electrons in a ferromagnetic crystal whilst keeping constant all the other parameters which influence ΔH.

III. EXPERIMENTAL WORK ON THE APPLICATION OF THE FERROMAGNETIC RESONANCE METHOD TO THE STUDY OF CATALYSTS

1. Study of Hydrogen Chemisorption

Various investigations of the chemisorption of hydrogen on Ni by magnetic methods have been reviewed by Selwood [4]. Magnetic methods can be applied to the study of chemisorption processes only when the ratio of the number of surface atoms to the number of atoms in the bulk is not too small (~ 0.6). This condition is satisfied for Ni crystals of less than 50 Å dimensions, i.e. for crystals which behave magnetically as superparamagnetics.

This size of Ni crystals is necessary also in studies of chemisorption by the ferromagnetic resonance method. The best catalyst from this point of view is Ni supported on SiO_2 or an alumina–silica, because Ni crystals of 10–50 Å size can be produced on these carriers. These were, indeed, the catalysts used by Selwood [17] to study the chemisorption of H_2 by the ferromagnetic resonance method. Catalysts containing 1–50% of Ni were prepared by saturating SiO_2 with a solution of $Ni(NO_3)_2$, followed by drying and reduction at 350°. The hydrogen chemisorbed during the reduction process was pumped off at 350°. The ferromagnetic resonance spectrum was recorded before and after exposure to hydrogen. Catalysts containing 10% Ni were examined in greatest detail: their ferromagnetic resonance spectrum before and after adsorption of hydrogen is reproduced in Fig. 14. The line width is unaffected (within experimental

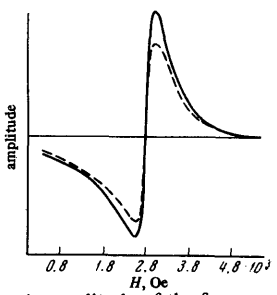

Figure 14. Change in amplitude of the ferromagnetic resonance line during adsorption of H_2 on Ni-SiO_2.[17] Continuous line—before adsorption; dashed line—after adsorption.

error) by the exposure to hydrogen, and remains at 470 ± 30 Oe, but the amplitude of the signal decreases by 15–25%. The g-factor, equal to 2.22, is also unaffected by the admission of hydrogen. As expected, the decrease in amplitude was a function of the particle size of the Ni. Thus, with a commerical catalyst of average Ni particle size 40 Å the decrease in amplitude was only 6%, and for the catalyst described above containing 10% Ni and having an average Ni particle size of 15 Å the decrease in amplitude was ~18%. Selwood showed that the decrease in amplitude was linearly related to the amount of hydrogen chemisorbed. Thus, the ferromagnetic resonance method qualitatively confirms the results obtained by static or low-frequency magnetic methods. However, Selwood points out that the main advantage of the ferromagnetic resonance method as compared with other magnetic methods is its very high sensitivity. He assumed that very small Ni crystals can be obtained by using catalysts with a low Ni content, and that these crystals will contain an extremely large number of surface Ni atoms, thus giving an enhanced change in the intensity of the ferromagnetic resonance signal.

Unfortunately, the sensitivity of the ferromagnetic resonance method is not such a simple problem. For measurements on catalysts containing relatively coarse Ni particles (>200 Å), the ferromagnetic resonance method offers no advantage over static magnetic methods of measuring the amount of ferromagnetic phase. If the concentration of Ni on the surface is decreased at the same time as the particle size, the sensitivity of the ferromagnetic resonance method does not increase, but actually decreases. We have already pointed out that low concentrations of small Ni particles on the surface produce a drastic broadening of the ferromagnetic resonance line due to the effect of dipole–dipole interaction. This substantial line broadening associated with low Ni concentrations on the carrier has in fact been observed in studies of Ni catalysts on charcoal [18]; the effect results in a loss of sensitivity, and imposes a limit on the application of the method to systems of this type. Furthermore, very small amounts of material (0.1–10 mg) are used for plotting ferromagnetic resonance spectra: quantitative adsorption data cannot be obtained under these conditions. Hence, there is no justification at the moment for the belief that the ferromagnetic resonance method is more sensitive in hydrogen chemisorption studies than the low-frequency permeameter method, which can accept large amounts of material (up to 10 g) and has an acceptable sensitivity. The real advantage of the ferromagnetic resonance method over other magnetic methods is the potential access to new information, in principle, on the structure and properties of Ni in catalysts, information which cannot be obtained by other methods.

A paper by Loy and Noddings [19] also describes a study of the interaction between Ni and hydrogen. These workers investigated the catalyst $NiCa_3(PO_4)_6$, used in the dehydrogenation of butene to butadiene. The interaction between hydrogen and the catalyst was analysed in two ways: 1) from the dependence of the amplitude of the ferromagnetic resonance signal upon the temperature of exposure of the catalyst to hydrogen, and 2) by saturation of the Ni with hydrogen at high temperatures, followed by desorption of the hydrogen at the same temperature.

The first method involved the following experimental procedure. The catalyst pellet was reduced for 15 min at the desired temperature, and the ferromagnetic resonance spectrum was recorded at room temperature. The specimen was next oxidised at the reduction temperature and the spectrum was again recorded. This oxidation–reduction cycle was repeated on the same pellet over the temperature range 400–800°.

In the second method the catalyst was reduced in a stream of hydrogen at 1100° for 30 min, the ferromagnetic resonance spectrum was measured, the hydrogen was pumped off at 1100° for 1.5 h, and the spectrum was again measured.

Fig. 15*a* shows the ferromagnetic resonance spectrum after an oxidation–reduction cycle by the first method. The line width for the reduced catalyst is 720 Oe, and $g = 2.2$. No signal is obtained after oxidation. The change in the relative intensity of the ferromagnetic resonance signal as a function of the temperature of hydrogen treatment is shown in Fig. 16. The authors interpret this behaviour by postulating the occurrence of two processes.

1. Catalysts reduced below 670° contain metallic Ni, produced by the reduction of Ni^{2+}, in an amount which increases with increase of reduction temperature, accompanied by a corresponding increase in the intensity of the ferromagnetic resonance signal.

2. Reduction of the catalyst above 670° leads to a decrease in signal intensity, due to the decreased magnetisation of the Ni following hydride formation in the bulk or on the surface of the Ni crystals.

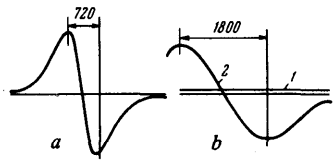

Figure 15. Resonance absorption curve for a nickel–calcium phosphate catalyst:
a) reduced at 680°; *b*) reduced at 1100° (*1*) and degassed at 1100° (*2*).

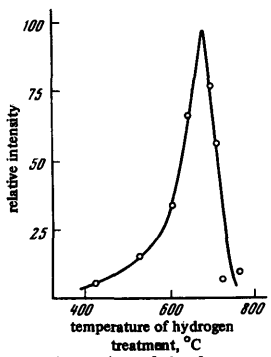

Figure 16. Relative intensity of the ferromagnetic resonance signal of a nickel–calcium phosphate catalyst as a function of the temperature of reduction.

Fig. 15*b* shows the ferromagnetic resonance spectra of a catalyst reduced at 1100° and degassed at 1100°. The reduced catalyst does not give a signal, but the outgassed catalyst gives a broad line ($\Delta H = 1800$ Oe) with $g = 2.55$. The authors suggest that reduction at 1100°C produces the diamagnetic nickel hydride, which is decomposed by evacuation at 1100° with regeneration of metallic nickel, which gives a ferromagnetic resonance signal. Thus, the conditions for the interaction of Ni with hydrogen chosen in this work are quite different from those of Selwood's work, in which hydrogen chemisorption was studied. Obviously, in Loy and Noddings' work nickel hydrides are formed, i.e. there is formation of bulk chemical compounds. Furthermore, at the high heat treatment temperatures used in this work sintering of the metallic nickel must be substantial, and yet the authors ignore this process in their subsequent discussion (analysed below).

2. Study of the Shape of Nickel Particles and of the Structure of Nickel Catalysts

The earliest application of the ferromagnetic resonance method was in a study of the structure of nickel catalysts prepared by the decomposition of Ni formate in sunflower oil in a stream of hydrogen[20]. X-Ray diffraction and magnetic studies of the catalysts were used to complement the ferromagnetic resonance spectra. It was shown that the *g*-factor calculated without applying corrections for the crystallographic magnetic anisotropy and for shape anisotropy was 2.22, i.e. the particles were spherical. In contrast to the behaviour of Raney nickel catalysts,[21] dehydrogenation does not increase the magnetisation and the intensity of the ferromagnetic resonance signal: on the contrary, it is accompanied by fragmentation (the particle size falling from 100 to 50 Å) and by a decrease in magnetisation (from 7.2 to 0.30). The dehydrogenated catalyst has a very labile structure consisting of finely divided Ni (width of the ferromagnetic resonance line 300 Oe), which undergoes extensive sintering at moderate temperatures.

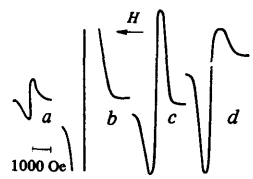

Figure 17. Ferromagnetic resonance spectra of heat treated nickel formate catalysts:
a) starting catalyst; *b*) catalyst sintered in air for 2 h at 300° (at the same amplification); *c*) catalyst sintered in vacuum for 4 h at 300°; *d*) catalyst sintered in air for 4 h at 300°C.

Fig. 17 shows the ferromagnetic resonance spectra of the formate catalyst, dehydrogenated by nitrobenzene, for various conditions of heat treatment. It is evident that sintering the catalyst in air at 300° (Fig. 17*b*) produces a sharp increase in the intensity of the signal. This is due to the fact that with a very labile and "loose" catalyst structure the growth of Ni particles, accompanied by an increase in magnetisation, is much faster than the oxidation of Ni to NiO. Typically, sintering the catalyst in a vacuum or in the air causes substantial line broadening (from 300 to 900 Oe), increase of particle size (from 50 to 200 Å), and increase of magnetisation (from 0.3 to 14.0), but sintering in the air additionally gives a sharply asymmetric line (Fig. 17*d*). As stated above, these processes are determined by non-uniform magnetisation of the sample (due to magnetic anisotropy, shape anisotropy, NiO impurities), which increases with increase of the Ni particle size.

Gasumura and Abe[22] have reported a study of the ferromagnetic resonance spectra of two Raney nickel catalysts, prepared by leaching a melt containing 49% Ni and vacuum heat treatment (10^{-3} mmHg) for 2 h at 70° and 300°. The catalyst prepared at 70° was active towards hydrogenation and had a magnetisation of 11.0; that treated at 300° was inactive with a magnetisation of 27.0. The ferromagnetic resonance spectra of both catalysts are shown in Figs. 18*a* and 18*b*. The line asymmetry of the catalyst heated at 70° is not due to anisotropy of the *g*-factor, as stated by the authors, but to shape anisotropy (see Fig. 7) or to magnetic

anisotropy. The question can be resolved by measuring the temperature dependence of the asymmetry coefficient of the line. In this case the asymmetry of the line is evidently associated with shape anisotropy, since sintering of the catalyst gives a symmetrical line with $g = 2.22$ (Fig. 18*b*). The increased magnetisation on sintering is due mainly to growth of the Ni particles, and not to the evolution of hydrogen. The lower catalytic activity of the catalyst heated at 300° evidently has the same explanation.

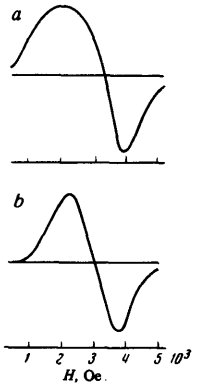

Figure 18. Ferromagnetic resonance spectra of Raney nickel catalysts[22]:
a) catalyst heated in vacuum at 70°C, $g = 2.09$; *b*) catalyst heated in vacuum at 300°C, $g = 2.22$.

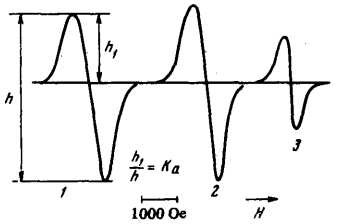

Figure 19. Temperature variation of the asymmetry coefficient (K_a) of the line for Ni–ZnO catalysts (49.5% Ni):
1) 20°; *2*) 100°; *3*) 220°C.

A similar increase in the symmetry of the line with a tendency of the *g*-factor towards the value 2.20 (characteristic of spherical particles), and increased magnetisation, was observed during the sintering of Ni prepared by chemical reduction with sodium hypophosphite[23]. A study has been reported[24] of the temperature dependence of the asymmetry coefficient of the ferromagnetic resonance line for Ni–ZnO catalysts. The results are given in Table 1 and Fig. 19. It can be seen that the line becomes more symmetrical as the measurement temperature is raised. Thus, the asymmetry of the ferromagnetic resonance line in this case is not due to shape anisotropy of the particles (since there is no sintering of the catalyst during the measurements) but to a steep temperature dependence of the Ni anisotropy constant (see Fig. 4), and hence to a decreased non-uniformity of magnetisation at higher measurement temperatures. It is obvious, therefore, that the existence of line asymmetry can be interpreted only as an indication

Table 1. Variation of the asymmetry coefficient of the ferromagnetic resonance line (K_a) with measurement temperature

Concentration of Ni, wt.%*	Catalysts reduced from oxides**					Concentration of Ni, wt.%	Catalysts reduced from hydroxides***				
	temperature dependence of K_a				*g*-factor		temperature dependence of K_a				*g*-factor
	20°	100°	220°	−196°			20°	120°	210°	−196°	
5.6	0.50	0.50	0.50	—	2.18	5.6	0.50	0.50	0.50	0.43	2.20
8.8	0.45	0.48	0.53	0.04	2.20	9.1	0.5	0.5	0.5	0.30	2.18
14.3	0.46	0.52	0.53	0.01	2.20	20.3	0.47	0.48	0.49	0.16	2.18
39.8	0.36	0.45	0.52	0.13	2.18	56.9	0.54	0.54	0.50	0.11	2.30
49.5	0.41	0.44	0.49	—	2.18	66.8	0.46	—	—	—	—
51.0	0.26	0.41	0.50	—	2.20	81.8	0.34	0.44	0.44	0.05	2.30
77.3	0.31	0.48	0.49	0.01	2.54	91.8	0.18	0.48	0.53	—	3.00

* Concentration of Ni quoted with allowance for partial reduction.
** Prepared by reduction from NiO–ZnO samples heated at 600°C.
*** Prepared by reduction from the hydroxides $Ni(OH)_2$–$Zn(OH)_2$ dried at 100°C.

of the presence of non-uniform magnetisation, but not of the origin of the non-uniformity. The underlying causes can only be established by a detailed study of the specimen using different methods, and in particular by observing the temperature variation of the shape of the ferromagnetic resonance line.

3. Interaction Between Ni Particles in Catalysts According to Ferromagnetic Resonance Data

The problem of the interactions within Ni particles and between particles was formulated on the basis of ferromagnetic resonance data by Loy and Noddings[19]. These workers measured the temperature dependence of the amplitude of the ferromagnetic resonance signal, and obtained the results summarised in Fig. 20. A curve of this

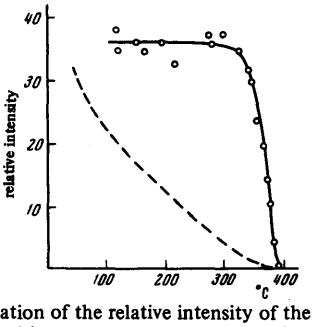

Figure 20. Variation of the relative intensity of the ferromagnetic resonance signal with measurement temperature for a nickel–calcium phosphate catalyst[19]. The dashed curve shows the shape of the thermomagnetic curve for finely divided nickel.

shape for the change in magnetisation with temperature is characteristic of coarsely divided Ni, but the authors state that coarse Ni particles could not have been present in their catalysts because the magnetisation disappears completely under the appropriate conditions in the presence of hydrogen, indicating[17] that the Ni particles must be very finely divided. But finely divided Ni particles should have a low Curie point (not 358°, as suggested by Fig. 20), and their thermomagnetic curve should have the shape of the dashed line in Fig. 20. Loy and Noddings explain these

anomalies by postulating that resonance methods measure transitions in individual domains, whereas static measurements encompass the whole particle including inter-domain interactions. In small particles this interaction is distorted by thermal energy, leading to abnormally low Curie points. The authors consider that the particle size and the influence of thermal vibrations are reflected only by the line width, and not by the Curie point. However, this explanation seems to be physically unsound for the following reasons.

1. There is not justification at all for associating the loss of magnetisation on exposing the catalyst to hydrogen at temperatures as high as 800–1100° with the presence of small particles. At those temperatures the interaction of hydrogen with nickel ceases to be a surface chemisorption effect, and involves the whole mass of the particle in formation of a bulk hydride phase, as the authors themselves point out. Obviously, as soon as the loss of magnetisation can be ascribed to the formation of a bulk phase of nickel hydride, it is no longer necessary to consider only very small nickel particles, and the same process can occur with coarse nickel crystals.

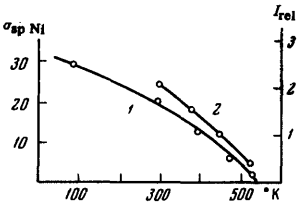

Figure 21. Temperature dependence of the saturation magnetisation (*1*) and of the relative intensity of the ferromagnetic resonance signal (*2*) for a Ni-ZnO catalyst (20.3% Ni).

2. With very small Ni crystals—complete demagnetisation under the influence of hydrogen is theoretically possible for a particle size < 10 Å—the concept of domains and domain boundaries (see Section II,4) loses physical significance, because such particles are not subdivided into domains. Therefore, the suggestion that in these particles the transitions within domains are characterised by resonance methods whilst static methods include interactions between domains is not physically justified. Both static and resonance methods should give the same type of change of magnetisation with temperature. This was actually demonstrated by the present writer [24] for an Ni–ZnO catalyst. Curve *1* of Fig. 21 was obtained from static measurements, and curve *2* shows the relative change of the integral intensity of the ferromagnetic resonance signal. It is evident that the two curves have entirely similar trends, i.e. that the presence of fine Ni particles in the catalyst is manifest in both static and resonance methods. The influence of various factors on the line width has already been treated in detail in previous Sections. Measurements on a single catalyst at a single temperature usually provide very little information on the underlying causes of the observed line width.

Data on the temperature dependence of the line width for a series of Ni–ZnO catalysts are set out in Table 2. All the catalysts show a characteristic decrease in line width with increase of temperature, and an increased line symmetry (Table 1). It follows that additional line broadening is due to magnetic crystallographic anisotropy rather than to shape anisotropy of the particles. The higher the measurement temperature, the lower is the magnetic anisotropy constant (see Fig. 4), and the less substantial is the line broadening due to this factor. As already pointed out above, from the point of view of magnetic anisotropy the line width is relatively insensitive to temperature until it begins to rise steeply on approaching the Curie point. Therefore, the opposite change of ΔH with temperature for Ni–ZnO catalysts must be ascribed to magnetic crystallographic anisotropy, and this effect should not be ignored in work with powdered materials.

Table 2. Variation of the width (ΔH) of the ferromagnetic resonance line with measurement temperature.

Concn. of Ni, wt.%, allowing for incomplete reduction	Catalyst reduced from oxides: temperature dependence of ΔH, Oe				ΔH, Oe after sintering*
	20°	100°	220°	−196°	
5.6	780	690	660	—	1700
8.8	780	720	660	1170	1320
14.3	750	660	660	1260	960
39.8	1050	780	660	1620	1350
49.5	1600	1250	680	1740	1800
51.0	1440	1080	690	3500	1860
77.3	2340	2040	1380	—	—

* Sintering in vacuum (10^{-5} mmHg) for 12 h at 410°C.

Since the line width measured at 220° is practically constant in catalysts containing 5.6–51% Ni (Table 2), the width is evidently determined by strong exchange interactions within the particles (particle size 400 Å) and relatively weak interactions between particles. Sintering of the catalysts causes increased magnetisation, growth of the Ni particles, and therefore also a greater influence of the anisotropy effect ($K_1 V \gg kT$) and considerable line broadening (Table 2). Simultaneously decreasing the size of the Ni particles on the carrier and their concentration produces considerable line broadening [18], obviously through dipole–dipole interaction. However, in the presence of a large number of fine Ni particles very close to each other the state of affairs can be quite different. Thus, with Ni particles prepared by decomposition of nickel formate in oil and having dimensions of the order of 40 Å, the line width was found [20] to be only 300 Oe. This value is even lower than the value reported [25] for colloidal Ni particles. Obviously, with high densities of small ferromagnetic particles in close proximity the dipole–dipole broadening is masked by the exchange interactions which tend to sharpen the line. Characteristically, the line width for this catalyst does not change on going to −196°, i.e. it is not determined by spin–lattice relaxation and magnetic anisotropy: it may be close to the true line width characteristic of the material.

Ni–Al_2O_3 catalysts have been investigated by Rubinshtein and coworkers [26]. Even small (5 wt.%) additions of Al_2O_3 enable a symmetrical ferromagnetic resonance signal to be observed ($g = 2.2$, $\Delta H = 1400$ Oe). Pure Ni under the same reduction conditions (350°C) gives a line so broad as to be almost impossible to plot (Figs. 22*a* and 22*b*). Reduction of the same catalyst at 450°C produces some line broadening ($\Delta H = 1550$ Oe) and above all an increase of the *g*-factor to 2.8. This is due to slight sintering of the Ni crystals, and to the associated increase in the non-uniformity of magnetisation, leading to line broadening

and a change in the g-factor. The effect is entirely analogous to the result obtained[19] for a nickel–calcium phosphate catalyst reduced at 1100°, and is further confirmation of the sintering processes which Ni undergoes at these temperatures. The major effect of small additions of Al_2O_3 on the ferromagnetic resonance spectrum of Ni is explained by a substantial increase in the disperseness of the nickel (60–100 Å). The structure of the catalyst may be depicted as Ni particles (60–100 Å in size) separated by thin layers of Al_2O_3. This structure is very stable towards sintering and very resistant to oxidation because of the slow diffusion of O_2 to the Ni particles, as shown by Rubinshtein and coworkers[26].

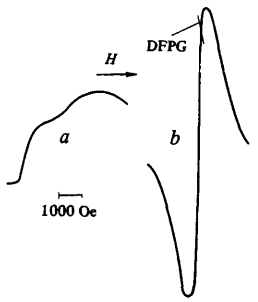

Figure 22. Ferromagnetic resonance lines for Ni and Ni–Al_2O_3 catalysts:
a) pure Ni; *b*) Ni–Al_2O_3 (~5% Al_2O_3).

We shall now briefly discuss the determination of the concentration of Ni, and its magnetisation, from ferromagnetic resonance data. Loy and Noddings[19] have computed the number of Ni atoms and the approximate domain size by comparing the area under the ferromagnetic resonance curve with the area under the curve of a *paramagnetic standard* ($MnSO_4.H_2O$). This procedure is, of course, physically quite unsatisfactory for quantitative calculations, because a ferromagnetic with the same number of atoms as a paramagnetic is subject to exchange forces giving rise to enormously greater values of the magnetisation. Even more unsatisfactory is the method proposed by Fasman[27], in which the relative integral intensities of ferromagnetic resonance lines are calculated by the formula $I = A(\Delta H)^2$, where A is the amplitude of the second derivative and ΔH is the line width. This formula is analysed, and the conditions under which it can be applied are discussed, in Refs. 6 and 28. It is used to calculate the concentration of unpaired spins in paramagnetic materials, by reference to a standard, in the case of *symmetrical lines*. For asymmetric lines the use of this formula is inadmissible, because it leads to considerable errors. The saturation magnetisation has been evaluated from ferromagnetic resonance data[9] by means of the formula

$$\mu''_{res}\,\Delta H = 4\pi\sigma_0$$

where μ''_{res} is the imaginary part of the dynamic permeability under resonance conditions, ΔH is the line width, and σ_0 is the saturation magnetisation of the sample.

Calculation of the change in relative intensity requires a double integration of the absorption line (when plotted in the form of the first derivative), followed by measurement of the area under the curve, which is proportional to the magnetisation.

As regards the quantitative determination of Ni in the catalysts, the problem is very much complicated by the fact that for a given number of Ni atoms in the sample the magnetisation (or area under the absorption curve) will be strongly dependent on the size of the particles formed by the Ni atoms. Therefore, each catalyst sample requires its own standard with the same size distribution of Ni particles. It is very difficult, of course, to fulfil this condition.

4. Interaction of the Metal with the Carrier

In recent years, the study of the structure and of the catalytic activity of supported metal catalysts has attracted increasing interest, and the problem has become a key one in catalysis. An important aspect of this problem is whether direct electronic interaction is present between the carrier and the metal, and whether the catalytic activity is thereby affected. Various workers have shown[29–32] that doping of the carriers (Al_2O_3, ZnO, MgO) with different cations (Li^+, Ga^{3+}) which affect their electrical conductivity produced a change in the catalytic activity of the deposited nickel. We shall not attempt a detailed analysis of these researches, and we shall consider only the physical effect which underlies these observations.

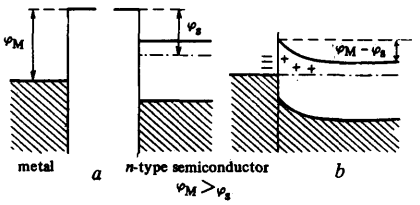

Figure 23. Energy level diagram for the contact between a metal and an n-type semiconductor:
a) before contact; *b*) after contact.

The physical effect is based on phenomena at the metal–semiconductor interface. Assume an n-type semiconductor of work function φ_s and a metal of work function φ_M, such that $\varphi_M > \varphi_s$ (see Fig. 23*a*). If the metal is brought into contact with the semiconductor, electrons from the semiconductor (at a higher chemical potential) will be transferred to the metal until the chemical potentials in the metal and the semiconductor are equal. As a result, the layer of semiconductor adjacent to the metal becomes depleted of current carriers and positively charged, and the metal layer becomes negatively charged. At the boundary, a potential barrier is formed (Fig. 23*b*): this barrier plays an essential role in rectifying contacts. An analogous model can be set up for the case of a metal deposited on a p-type semiconductor. This transfer of electrons to the metal from the semiconductor (metal–n-type semiconductor boundary, $\varphi_M > \varphi_s$) or to the semiconductor from the metal (metal–p-type semiconductor boundary, $\varphi_M < \varphi_s$) is invoked by the authors of these papers to account for the change in catalytic activity of the Ni deposited on variously doped

carriers. And yet, the reality of this transfer in catalysts has not so far been demonstrated. Can the ferromagnetic resonance method be applied to the solution of this problem? We have already pointed out that the true line width is determined by the interaction between the ferromagnetic system of electrons and the conduction electrons. Hence, if the metal is depleted or enriched of electrons, the relaxation time (and therefore also the line width) can be expected to change. Thus, the experiment consists in determining changes in line width for Ni deposited on carriers having different electrical properties. However, such an experiment is very difficult to realise, because (as stated above) the line width in systems of the catalyst type is not determined exclusively by relaxation processes. The experiment requires that the Ni on the various carriers should have: 1) an identical size distribution of Ni particles; 2) identical particle shape, so as to exclude shape anisotropy; 3) identical and preferably low concentration of Ni on the carrier, so as to avoid interaction between Ni particles.

The measurements should be made at high temperatures, in order to avoid line broadening through magnetic crystallographic anisotropy. The Ni particles should have the greatest possible degree of disperseness, but such as to allow resonance to be observed, since the effect will be most pronounced in this case. Of course, it will not be easy to fulfil all these conditions, but qualitatively new information on the structure of metallic catalysts on carriers can be expected from work of this type.

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The ferromagnetic resonance method has recently begun to be applied to the study of ferromagnetic catalysts in parallel with the various magnetic methods of investigating paramagnetic and ferromagnetic catalysts. The method is capable in principle of producing qualitatively new information on the properties of ferromagnetic catalysts, which cannot readily be obtained by other methods: 1) on the interactions within and between ferromagnetic particles; 2) on the structure of ferromagnetic catalysts and its dependence on various influences; 3) on the interaction between the catalyst and various adsorbents; 4) on the shape of the ferromagnetic particles; 5) on the nature of the interaction between the ferromagnetic metal and the carrier.

We may hope that extensive application of this method will result in an even closer approach to an understanding of the structure of real catalysts and to the development of a modern theory of catalysis.

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on the reactivity of organophosphorus insecticides with cholinesterase has assisted in the elucidation of the mechanism of their physiological action, which is extremely important for the understanding of a whole series of biochemical processes.

Your amazing capacity for work and keen intellect combined with encyclopaedic knowledge leave us no doubt about further successes of the school which you have established. We value greatly the opportunity of working with you.

We wish you health and new creative successes in your scientific and public activities.

Editorial Board of "Uspekhi Khimii"

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Oxidation of Benzene

E.T.Enisov and D.I.Metelitsa

The review gives a systematic account of studies on the oxidation of benzene by different methods—with oxygen in the gas phase, with Fenton's reagent in aqueous solution, under the action of light and penetrating radiation, and also catalytic oxidation in aqueous solution. Particular attention has been paid to the mechanism of the oxidation of benzene; the main experimental evidence for individual mechanisms is discussed and unlikely schemes are criticised. Kinetic data and the mechanism of the catalytic oxidation of benzene to phenol with oxygen in aqueous solution in the presence of iron and copper ions which follows from them are discussed in detail. The bibliography incorporates 120 references.

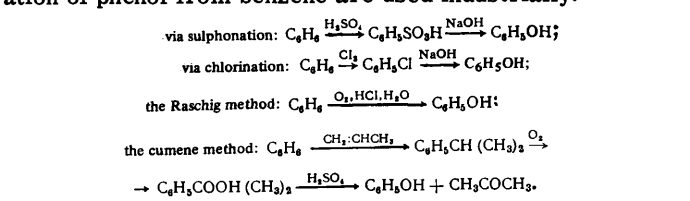
CONTENTS

I.	Introduction	656
II.	Gas-phase oxidation of benzene	656
III.	Oxidation of benzene with Fenton's reagent	657
IV.	Radiation-chemical and photochemical oxidation of benzene	658
V.	Initiated liquid-phase oxidation of benzene	660
VI.	Catalytic oxidation of benzene in aqueous solution	660
VII.	Other methods for the oxidation of benzene	664

I. INTRODUCTION

Benzene differs sharply from other hydrocarbons by its high stability with respect to oxidation, which is due to its structure. Hydrocarbons are known to be oxidised by a free-radical mechanism, the reaction including a stage involving the homolytic abstraction of a hydrogen atom. The high stability of the C–H bond in benzene (102 kcal mole^{-1}) is one of the reasons for its stability. No less important is another factor, namely the major role played in the oxidation of hydrocarbons by hydroperoxides, which break down into free radicals and initiate further chain oxidation. The corresponding hydroperoxide is not known for benzene and attempts to synthesise it have proved unsuccessful, and it appears that it does not exist as a stable molecular compound. The absence of a hydroperoxide as the species initiating the reaction does not favour rapid oxidation. Finally, it is very significant that the oxidation of benzene yields phenol and products of its further oxidation, which behave as inhibitors of chain reactions involving the oxidation of hydrocarbons. All these factors explain the stability of benzene with respect to oxidation.

The oxidation of benzene to phenol is of practical importance. Nowadays the following methods for the preparation of phenol from benzene are used industrially:



These procedures, including the cumene method which is the most economical, consist of many stages. Therefore the development of an effective single-stage process is important. As will be seen from the present review, under certain conditions it is possible to oxidise benzene to phenol with a fairly high yield. The theoretical possibility of oxidising benzene to phenol under mild conditions is a consequence of the existence of enzymes which can, for example, oxidise phenylalanine to tyrosine.

II. GAS-PHASE OXIDATION OF BENZENE

The first studies on the oxidation of benzene with molecular oxygen in the gas phase were performed in the 1920's. The gas-phase oxidation of benzene takes place at 500–700°C.[1-31] The oxidation yields phenol, resins, carbon monoxide, and carbon dioxide. At these high temperatures the oxidation of benzene is accompanied by its cracking on the wall of the reaction vessel. Glass packing favours the cracking process[27]. As a result of cracking, low-molecular hydrocarbons (methane, ethylene, acetylene, etc.) are formed together with the oxidation products[19,20,27]. In a number of investigations homogeneous catalysts, such as hydrogen chloride, nitrogen dioxide, and iodine were used. As an example, one may quote the experiments with iodine in which the introduction of 0.02% of iodine into air at 604°C increased the yield of phenol from 40.4% (without iodine) to 56.5% with respect to unreacted benzene[12]. In order to accelerate the oxidation of benzene, atomic oxygen obtained in an electric discharge has also been used[13,21,22]. The oxidation of benzene has been stimulated by readily

oxidisable organic compounds: cyclohexane, cyclohexanol, cyclohexanone, n-hexane, aniline, cyclohexene, etc.[15,23,28].

Photochemical oxidation of benzene at room temperature leads to the formation of phenol and a peroxide[24]. The phenol undergoes further photochemical decomposition.

The heterogeneous oxidation of benzene to maleic anhydride on vanadium pentoxide is an industrial method. The rate-limiting stage of this process is the heterogeneous oxidation of benzene to phenol, which is then rapidly oxidised to quinone and the latter is oxidised to maleic anhydride[8]. Table 1 gives the benzene oxidation conditions and the yields of phenol obtained in a number of the most interesting studies.

Table 1. Oxidation of benzene.

Oxidation conditions	Oxidation products	Yield of phenol, %	References
Benzene–air mixture, 300–500°C	phenol, biphenyl, maleic and formic acids	0.5—1.0 by weight	19,20
Benzene–air, 520–685°C, column without packing	phenol, resins, CO, CO_2, CH_4	20—26	27
Benzene–air, packed column	phenol, resins, CO, CO_2, CH_4, C_2H_2	16—18	
$O_2 + N_2$ + benzene, 660°C	phenol, resins	30	14
Atomic oxygen + benzene, 180–230°C		4.5—27	22
Atomic oxygen + benzene	phenol, biphenyl, CO, CO_2	43	13
Benzene–air, I_2(0.02%), 604°C	phenol, biphenyl	56.5	12
5% O_2 + benzene, 400–500°C	phenol, resins	to 75	5
Chromium, molybdenum, vanadium, and tantalum oxides			
Benzene–air, V_2O_5, 316°C	phenol, maleic acid	1.9	16
Benzene + cyclohexane (10%), 585°C		62	23
Benzene + readily oxidisable organic substances, 400°C	phenol, CO, CO_2, resins, CH_4, C_2H_2	20—26	28
Benzene + cyclohexane (0.2–0.3%), 449°C		30	15

The kinetics of the gas-phase oxidation of benzene were investigated by Ioffe[26–30] and Norrish et al.[31] The kinetic curves for the disappearance of benzene and the accumulation of phenol have the S-shape characteristics of auto-oxidation processes. In the initial period the reaction kinetics are described by the following equation: conversion = const. $\times e^{\varphi t}$, where φ = const. $\times e^{-32\,000/T}$ at 660–685°C for $(C_6H_6):(O_2) = 2:1$.[30] It is suggested that the acceleration of the reaction occurs as a result of the oxidation of side products such as methane, ethylene, etc.[30] The following mechanism has been proposed for the initial stage of the oxidation[30,31]:

$$C_6H_6 + O_2 \rightarrow C_6H_5^{\cdot} + HO_2^{\cdot},$$
$$C_6H_5^{\cdot} + O_2 \rightarrow C_6H_5OO^{\cdot},$$
$$C_6H_5OO^{\cdot} + C_6H_6 \rightarrow C_6H_5O^{\cdot} + C_6H_5OH,$$
$$C_6H_5O^{\cdot} + C_6H_6 \rightarrow C_6H_5OH + C_6H_5^{\cdot},$$
$$C_6H_5^{\cdot} + C_6H_5^{\cdot} \rightarrow C_6H_5{-}C_6H_5.$$

The available experimental data are still insufficient to decide whether this mechanism of the gas-phase oxidation at high temperatures should be accepted or rejected. One can only note that the reaction of phenoxy-radicals with benzene is endothermic to the extent of 17 kcal mole^{-1} and should be extremely slow. The reactions of phenoxy-radicals with O_2, benzene ("addition"), and phenyl radicals should be faster.

Phenol is an intermediate and undergoes further oxidation. The oxidation of phenol was investigated by Ioffe at 650°C and a mechanism was proposed for the oxidation of phenol in the presence of benzene (RH is benzene)[26]:

$$C_6H_5OH + R^{\cdot} \rightarrow C_6H_4OH^{\cdot} + RH,$$
$$C_6H_4OH^{\cdot} + O_2 \rightarrow HOC_6H_4OO^{\cdot},$$
$$HOC_6H_4OO^{\cdot} + RH \rightarrow HOC_6H_4OH + RO^{\cdot},$$
$$C_6H_4OH^{\cdot} + R^{\cdot} \rightarrow RC_6H_4OH.$$

In this mechanism the first reaction, the removal of H from the C–H bond in phenol, is doubtful. The weakest bond in the phenol molecule is O–H and this should in fact be the point of attack by the radical on the phenol molecule which yields a phenoxy-radical.

III. OXIDATION OF BENZENE WITH FENTON'S REAGENT

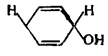
Fenton's reagent (aqueous solution of ferrous sulphate and hydrogen peroxide) is a source of hydroxy-radicals and is used for the oxidation of organic compounds[32–45]. In the absence of a substance undergoing oxidation, hydrogen peroxide breaks down as a result of the following reactions[41,45]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-},$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+},$$
$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-},$$
$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+},$$
$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot},$$
$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-} \overset{H^+}{\rightleftarrows} H_2O_2.$$

According to Baxendale et al.[46], the rate constant is $k = 1.8 \times 10^9 \exp(-10\,000/RT)$ litre mole^{-1} s^{-1}. In the oxidation of benzene with Fenton's reagent the benzene molecule is attacked by hydroxy-radicals. The oxidation products are phenol and biphenyl (in the presence of oxygen, biphenyl does not form). In the first studies on the oxidation of benzene[33,37] the following reaction mechanism was put forward:

$$PhH + HO^{\cdot} \rightarrow Ph^{\cdot} + H_2O,$$
$$Ph^{\cdot} + Fe^{3+} + HO^{-} \rightarrow PhOH + Fe^{2+},$$
$$Ph^{\cdot} + Ph^{\cdot} \rightarrow Ph{-}Ph.$$

If the oxidation involves the removal of a hydrogen atom from the benzene molecule, an isotope effect should be observed in the oxidation of deuteriated benzene. However, there is no isotope effect in the oxidation of benzene with Fenton's reagent[41]. Dixon and Norman[45] investigated by the ESR method the free radicals formed in the systems H_2O_2–Ti^{3+} and H_2O_2–Ti^{3+}–benzene and established that in the presence of benzene hydroxyl radicals vanish and new radicals appear, to which the following structure is attributed:

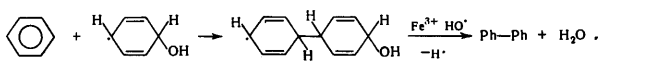


i.e. hydroxyl radicals add to benzene. The existence of the above radicals was also demonstrated spectroscopically[47]; the rate constant for the addition of HO$^{\cdot}$ to benzene has been calculated as 4.3×10^9 litre mole^{-1} s^{-1} (at 23°C). The high rate of addition of free hydroxy-radicals to benzene and the absence of an isotope effect are evidence that the oxidation of benzene with Fenton's reagent begins with the addition of OH$^{\cdot}$ to the benzene molecule:

$$C_6H_6 + HO^{\cdot} \rightarrow C_6H_6OH^{\cdot}.$$

The radical $C_6H_6OH^{\cdot}$ is then oxidised to phenol by the reaction with Fe^{3+} and HO$^{\cdot}$. Together with the oxidation to

phenol, this radical probably interacts with benzene and the product of such interaction is oxidised to biphenyl:



In the presence of oxygen the radical $C_6H_7O^{\cdot}$ is oxidised to phenol by the reaction with O_2 and this reaction is probably so fast that it successfully competes with the addition of $C_6H_7O^{\cdot}$ to benzene; this is why biphenyl does not form in the presence of oxygen. However, one cannot exclude the possibility that, as the temperature is raised, the reaction involving the "adhesion" of $HO^{\cdot}$ to benzene begins to be accompanied to a slight extent by the reaction involving the abstraction of a hydrogen atom. This is shown by the increase of the isotope effect: $k_H/k_D = 1.25$ (at 20°) and $k_H/k_D = 1.37$ (at 70°C) in the oxidation of a mixture of ordinary and deuteriated benzene with Fenton's reagent[48].

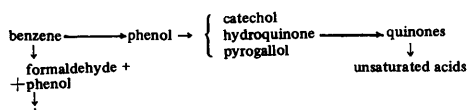
Aromatic compounds can be hydroxylated not only with Fenton's reagent but also with systems such as $Fe^{2+}-O_2$ and $Ti^{3+}-O_2$, but in such systems the hydroxylating agent is not $HO^{\cdot}$ but probably[49] the $HO_2^{\cdot}$ radical. For example, in the hydroxylation of *N*-acetanilide with the reagent hydrogen peroxide–iron(II) complex of EDTA (in this system the reactive species is $HO^{\cdot}$) the following mixture of isomeric *N*-acetamidophenols is obtained: *ortho*-isomer 46.5%, *meta*-isomer 2.5%, and *para*-isomer 51%. On the other hand, hydroxylation of *N*-acetanilide by the system $Fe^{2+}-O_2$ or $Ti^{3+}-O_2$ leads to a mixture of 35% of the *ortho*-isomer, 33% of the *meta*-isomer, and 32% of the *para*-isomer. This is evidence that *N*-acetanilide molecules are not attacked by hydroxy-radicals but by another species (for example $HO_2^{\cdot}$ radicals).

IV. RADIATION-CHEMICAL AND PHOTOCHEMICAL OXIDATION OF BENZENE

Much work has been done on the oxidation of benzene in aqueous solutions initiated by radiation of various kinds[50–71]. When a solution of benzene in water containing Fe^{3+} ions is irradiated with the light of the mercury lamp ($\lambda = 313$ nm), phenol, biphenyl, and Fe^{2+} ions are formed[50]. The addition of Cu^{2+} ions reduces the fraction of biphenyl. A mechanism has been suggested in which the hydroxy-radical removes a hydrogen atom from the benzene molecule. The results of the oxidation of benzene with Fenton's reagent convincingly demonstrate the addition of $HO^{\cdot}$ to benzene. Therefore the following mechanism can be suggested for the oxidation of benzene by Fe^{3+} ions:

$$Fe^{3+}_{aq} + h\nu \rightarrow Fe^{2+} + H^+ + HO^{\cdot},$$
$$HO^{\cdot} + C_6H_6 \rightarrow C_6H_7O^{\cdot},$$
$$C_6H_7O^{\cdot} + Fe^{3+} \rightarrow C_6H_5OH + Fe^{2+} + H^+,$$
$$C_6H_7O^{\cdot} + Cu^{2+} \rightarrow C_6H_5OH + Cu^{1+} + H^+,$$
$$C_6H_7O^{\cdot} + C_6H_6 \rightarrow HOC_6H_6{-}C_6H_6 \xrightarrow{Fe^{3+}} C_6H_5{-}C_6H_5 + H_2O + Fe^{2+} + H^+.$$

The oxidation of benzene in aqueous solution in an ultrasonic field yields phenol, which readily reacts further by the mechanism[52]

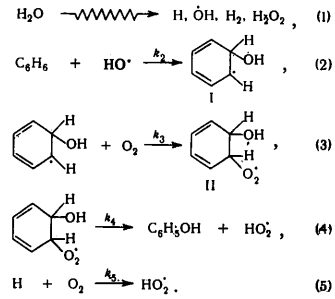


The radiolysis of aqueous benzene solutions under the action of cobalt-60 γ-rays has also been investigated[54–64]. At room temperature in the absence of oxygen oxidation in the two-phase system benzene–water takes place due to the water radiolysis product – H_2O_2, $HO^{\cdot}$, and $HO_2^{\cdot}$. The yields of phenol are slight: 2.64–2.94 m mole litre^{-1} kr^{-1}.[54,55] In the presence of oxygen the radiation-yield of phenol increases and reaches $G = 2$ molecules/100 eV. Proskurin and Barelko[55] established for the first time that the addition of Fe^{2+} or Fe^{3+} ions increases the yield of phenol to $G = 6$ and investigated the oxidation of benzene (under the action of γ-rays at an oxygen pressure of 10 atm) over a wide temperature range, between 20° and 220°C. The main products of the radiolysis of water–benzene mixtures (water : benzene = 32 : 1) under these conditions are phenol and a resin. The maximum yield of phenol at 200°C is 0.035 M with simultaneous formation of 0.025 M resin. The resin contains both phenolic derivatives and polyphenyls. Above 200°C the yield of phenol falls. When irradiation is stopped, the reaction continues with self-acceleration. The authors suggest that at high temperatures the oxidation of benzene is a branched-chain process.

The oxidation of benzene with X-rays yields phenol, biphenyl (in the absence of oxygen), hydrogen peroxide[68], and dialdehydes[69]. In the absence of oxygen the radiation yields G of the main oxidation products are 0.34 for phenol, 0.55 for biphenyl, 0.60 for hydrogen, and more than 0.60 for hydrogen peroxide. In the presence of oxygen or Fe^{2+} and Cu^{2+} ions the yield of phenol increases.

It has been shown[69] that phenol and dialdehydes are formed at the same time and approximately in the same amounts: G(phenol) = 1.8 and G(dialdehydes) = 1.5.

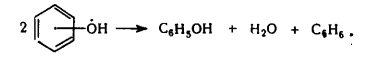
Let us now consider the mechanism of the radiolysis of aqueous benzene solutions[62,69]:



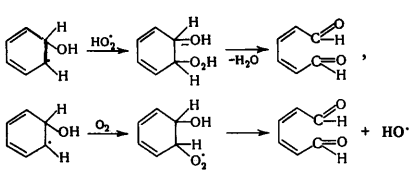
Reaction (2) is faster than reaction (3). Dorfman et al.[62] measured the rate constants k_2 and k_3 at 23°C:

$$k_2 = (4.3 \pm 0.9) \times 10^9 \text{ litre mole}^{-1}\text{ s}^{-1},$$
$$k_3 = (5.0 \pm 0.6) \times 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}.$$

The mechanism shows that phenol forms by the oxidation with oxygen of radicals (I) and that at the same time the radicals disproportionate[41,69]:



It is more logical to assume that reactions (3) and (4) take place in one stage. The formation of dialdehyde together with phenol can take place by the following hypothetical reactions[64,70]:

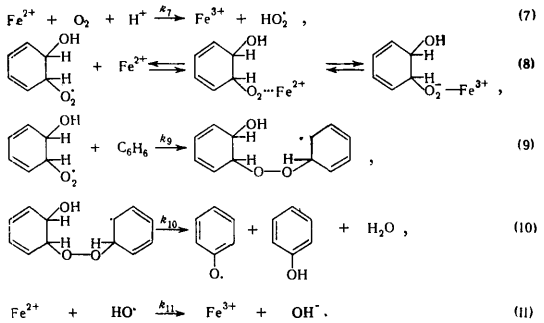


Thus, regardless of the source of radiation, the oxidation of benzene is initiated by the water radiolysis products HO· and $HO_2^·$. The mechanism of the oxidation of benzene is similar to that of the oxidation by Fenton's reagent: an HO· radical adds to benzene and the resulting radical is then oxidised with oxygen to phenol and other products. Some workers believe[71] that the oxidation of benzene under the action of radiation is suitable for the manufacture of phenol, particularly when iron ions are added. However, a considerable disadvantage of the radiation-chemical oxidation is the formation of a large amount of resins by the condensation of phenol and side products. Catechol, hydroquinone, hydroxybenzoic acids, maleic acid, and other compounds are formed in small amounts together with the resins.

As already noted several times, the addition of Fe^{2+}, Fe^{3+}, and Cu^{2+} ions in small amounts (at concentrations between 10^{-4} and 10^{-3} M) in the radiation-induced oxidation of benzene greatly increases the yield of phenol. Quite recently a group of Japanese investigators used the catalytic effect of iron and copper ions for the radiation-catalytic oxidation of benzene[72-79]. Benzene was oxidised in aqueous solutions of $FeSO_4$, $FeCl_2$, $CuCl_2$, and $Fe_2(SO_4)_3$ at concentrations between 10^{-4} and 0.1 M. At an oxygen pressure of 30 atm the reaction mixture was irradiated with cobalt-60 γ-rays for 25 min at different temperatures ranging from 100° to 200°C. When the reaction is carried out in the presence of Fe^{2+} ions, the maximum yield of phenol is 27 mg per ml of benzene, i.e. 2.5%. In the presence of Cu^{2+} ions, 1 ml of benzene yields 40 mg of phenol, i.e. 3.7% relative to the initial benzene. Biphenyl is not formed in the presence of iron and copper ions. It has been established that ferrous sulphate ensures a high yield of phenol both with and without γ-irradiation. In catalysis by Fe^{3+} ions considerable amounts of phenol are formed only on γ-irradiation; without it the yield of phenol is appreciable only at high temperatures (in excess of 180°C). In catalysis by cupric sulphate the yield of phenol is fairly high, both with and without irradiation[74] above 180°C. The catalytic effect of iron and copper chlorides is less than that of the corresponding sulphates[73,74]. The reaction is greatly influenced by the purity of the benzene; impurities such as toluene and thiophen increase the yield of phenol[75]. The addition of SO_4^{2-} ions greatly reduces the amount of phenol formed. When copper filings are introduced into the reaction vessel, the yield of phenol increases. An increase of the concentration of cupric sulphate from 10^{-4} M to 10^{-2} M at 198°C also increases the yield of phenol.

Phenol is the main reaction product but dihydroxybenzenes and also carbon dioxide, acetaldehyde formaldehyde, acetone, acetic acid, formic acid, and maleic acid are formed with it in small amounts (about 10^{-4} M).[77] All these compounds are formed as a result of the oxidation of phenol[76]. This conclusion was arrived at after the investigation of the products of the oxidation of phenol under the same conditions as those in the oxidation of benzene. All the compounds enumerated above were detected in the oxidation of phenol.

The study of the migration of oxygen with the aid of oxygen-18 shows that oxygen is incorporated into phenol both from water[78] and from O_2. In the oxidation of an equimolar mixture of benzene and hexadeuteriobenzene isotope analysis yielded $k_H/k_D = 1.2$. The low isotope effect suggests that a hydrogen atom is removed not from the benzene molecule but from a free radical, for example $\dot{C}_6H_6OH$. On the basis of experimental and literature data, Japanese investigators have suggested a mechanism for the oxidation of benzene under the action of γ-irradiation and in the presence of iron and copper ions. Without reservations, they extend the mechanism of radiation-induced initiation [reactions (1)–(5)], adopted for room temperature, to the high-temperature range:



(7)

(8)

(9)

(10)

(11)

At 25°C and pH 2 $k_{11} = 2.6 \times 10^8$ litre mole^{-1} s^{-1}.[80] It has been stated[81] that at 25°C k_2 is greater by a factor of 3.2 than k_{11}.

$$Fe^{2+} + H_2O_2 \xrightarrow{k_{12}} Fe^{3+} + OH^- + HO· . \quad (12)$$

At 150°C $k_{12} = 6.6 \times 10^{-3}$ litre mole^{-1} s^{-1} and is therefore smaller than k_2.[82] If the catalyst is Fe^{3+} or Cu^{2+} ions, then reaction (13) is the initiating process:

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO· . \quad (13)$$

In a number of studies the possibility of this reaction has been demonstrated[83,84]. According to the above mechanism, the role of the Fe^{2+} ion is determined by reaction (7), which leads to the formation of $HO_2^·$ radicals. It is also suggested that Fe^{2+} ions stabilise the peroxy-radicals by reaction (8) and make possible the occurrence of reaction (9). As mentioned above, the reaction of $C_6H_7O·$ radicals with O_2 takes place in one step. Therefore reactions (8)–(10) seem to be extremely unlikely and are superfluous in the mechanism. The inhibiting effect of Cl^- on the oxidation of benzene can be accounted for by the destruction of HO· radicals by the reaction

$$Cl^- + HO· \xrightarrow{k_6} Cl· + OH^- . \quad (6)$$

At 25°C $k_6 = 1.8 \times 10^8$ litre mole^{-1} s^{-1} (at pH 2). In 0.8 N sulphuric acid k_6 is greater by a factor of eight[80], while $k_2 = (4.3 \pm 0.9) \times 10^9$ litre mole^{-1} s^{-1} at 23°C. If the same temperature variation of k_2 and k_6 is assumed, then reactions (1) and (6) may compete at high temperatures.

Japanese investigators believe the oxidation of benzene to be a branched-chain process and on the basis of literature data[85] suggest the following branching mechanism:

$$PhO· + PhH \rightarrow PhOH + Ph· , \quad (14)$$

$$Ph· + O_2 \rightarrow PhO_2^· , \quad (15)$$

$$PhO_2^· + PhH \rightarrow PhO_2H + Ph· , \quad (16)$$

$$PhO_2H + Fe^{3+} \rightarrow PhO_2^· + Fe^{2+} + H^+ , \quad (17)$$

$$PhO_2H + Fe^{2+} \rightarrow PhO· + Fe^{3+} + OH^- , \quad (18)$$

$$PhO_2H = PhO· + HO· . \quad (19)$$

This mechanism is open to a number of significant objections. Reaction (14) cannot occur at an appreciable rate, since PhO· radicals show little activity and the C–H bond in benzene is strong. The reaction is endothermic (–17 kcal mole^{-1}) and cannot compete successfully to any extent with other reactions of phenoxy-radicals, such as

oxidation and addition to benzene. The hydroperoxide PhOOH does not exist as a molecular compound (particularly at a high temperature). Therefore all the reactions involving its participation must be excluded. The mechanism of the acceleration of the oxidation of benzene in the presence of iron and copper ions is discussed in greater detail in the section dealing with the catalytic oxidation of benzene.

V. INITIATED LIQUID-PHASE OXIDATION OF BENZENE

Various methods for the oxidation of benzene in aqueous solutions were discussed above. It has been shown[86,87] that the oxidation of liquid benzene to phenol under pressure below the critical temperature (t_{cr} = 288°C) is possible in principle. The oxidation was carried out in an autoclave at 230–270°C and a pressure of 50 atm. The oxidation results in the formation of phenol and resins.

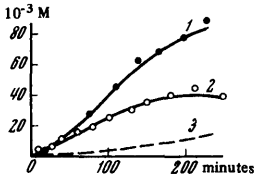


Figure 1. Kinetic curves for the accumulation of phenol at 250°C: *1*) in the experiment with continuous initiation by nitrogen dioxide; *2*) in the experiment with initial 40 min gas-phase initiation; the dashed curve indicates the accumulation of phenol in the experiment without initiation.

Table 2. Initiated oxidation of benzene.

t, °C	Conditions	Rate of formation of phenol, 10^{-3} mole litre min^{-1}	Phenol, mole %	Degree of oxidation, wt. %
250	No additive	0.07	0.16	0.7
230	2% C_6H_{12}	0.18	0.23	6.5
250	1% $C_6H_{10}O$	1.70	0.50	6.0
250	NO_2 continuous	0.49	0.80	5.3
250	NO_2 40 min	0.23	0.33	2.0
250	NO_2 + 1% C_6H_{12}	0.31	0.48	2.7
267	NO_2 continuous	0.88	1.10	4.0

The reaction takes place with self-acceleration, the concentration of phenol tending to a limit during the reaction. In the absence of initiating effects the maximum concentration of phenol at 250°C is 1.8×10^{-3} M and is attained 6 h after the start of the reaction. The oxidation of benzene can be stimulated by the introduction of readily oxidisable substances (cyclohexane, cyclohexanone) and by passing through the system nitrogen dioxide (gaseous initiator) together with air. Fig. 1 presents kinetic curves for the accumulation of phenol in experiments with nitrogen dioxide (2% NO_2 in the 1 : 1 N_2–O_2 mixture). Nitrogen dioxide accelerates the reaction and increases the amount of phenol formed. The results of the experiments are presented in Table 2.

The available data are so far insufficient for the discussion of a concrete mechanism of liquid-phase oxidation of benzene. However, the observed features of the kinetics indicate a free-radical oxidation mechanism (possibly of a chain type). These include the accelerating effect on the oxidation of benzene of the addition of substances readily oxidisable by a chain mechanism such as cyclohexane and cyclohexanone, the powerful effect of nitrogen dioxide which accelerates the oxidation of other hydrocarbons, and the S-shaped kinetic curves for the accumulation of phenol, which is a characteristic of chain auto-oxidation reactions. It should be noted that the oxidation of benzene is a self-inhibiting process, as shown by experiments where the initiation of this reaction by nitrogen dioxide was interrupted (Fig. 1).

VI. CATALYTIC OXIDATION OF BENZENE IN AQUEOUS SOLUTION

The possibility of the oxidation of benzene in aqueous solution at 170–200°C in the presence of iron and copper ions was established by Japanese investigators, who obtained interesting experimental data on this process[72-79,88].

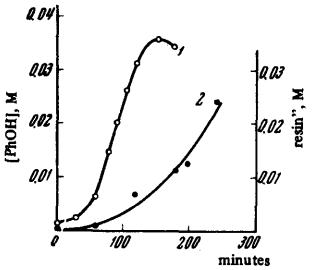


Figure 2. Kinetic curves for the accumulation of phenol (curve *1*) and resins (curve *2*) at 200°C and an air pressure of 35 atm in the presence of 0.012 M Cu^{2+} and 5 ml of benzene; the content of the $C_6H_4O_4$ resins (mole $litre^{-1}$) is plotted.

A detailed study of the kinetics and mechanism of this reaction has been made[89-94]. Benzene dissolved in water (at 185°C the solubility of benzene in water is 0.21 mole $litre^{-1}$) was oxidised with oxygen in an autoclave under pressure. In the presence of iron and copper ions benzene was scarcely oxidised at 185–200°C; Co^{2+}, Mn^{2+}, and Ti^{3+} ions do not catalyse the oxidation of benzene. In the presence of copper and iron ions benzene was oxidised fairly rapidly with formation of phenol. An appreciable quantity of phenolic resin with the elemental composition $C_6H_4O_4$ (Fig. 2) and a small amount of low-molecular products (acetaldehyde, formaldehyde, acetone, acetic acid, and carbon dioxide) were formed together with phenol[92]. The low-molecular products are formed as a result of the oxidation of phenol[76]. The catalytic oxidation of benzene is an autocatalytic reaction[89,92] (Fig. 2). The kinetics of phenol accumulation obey the equation for autocatalysis of the second kind: $dx/dt = k(1 - x)x^2$, where $x = [C_6H_5OH]/[C_6H_5OH]_{max}$. Phenol is an intermediate in this reaction, as can be clearly seen from experiments in which various

amounts of phenol were introduced into the initial benzene (Fig. 3). If the initial concentration of phenol is less than the maximum concentration, phenol accumulates, but if it is greater the concentration of phenol falls. It follows from the kinetic curve for the accumulation of phenol and the resin (Fig. 2), that the latter does in fact form as a result of the oxidation of phenol. Experiments with the introduction of phenol at the beginning of the reaction (Fig. 4) showed that phenol is the main product responsible for the autocatalysis of the reaction[92]. Surprisingly, the accumulation of phenol accelerates the oxidation of the initial benzene (usually in hydrocarbon oxidation reactions phenol behaves as an inhibitor).

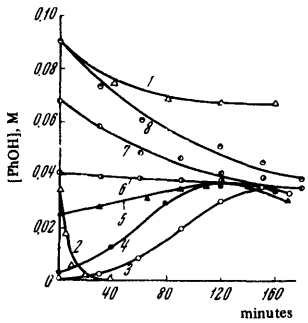


Figure 3. Kinetic curves for the accumulation and consumption of phenol at 200°C and a pressure of 35 atm (50% O_2) in the presence of 0.0125 M $CuSO_4$:
1) oxidation of phenol in benzene; *2*) oxidation of phenol in aqueous cupric sulphate without benzene; *3*)-*8*) kinetic curves for the accumulation and consumption of phenol in aqueous cupric sulphate solution in the presence of benzene (5 ml) in experiments with initial addition of phenol.

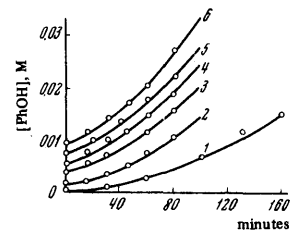


Figure 4. Initial sections of the kinetic curves for the accumulation of phenol at 200°C at pH 1.2 in the presence of 5 ml of benzene and 90 ml of 0.006 M Fe^{3+} solution and different concentrations of added phenol (M):
1) no phenol added; *2*) 0.0018; *3*) 0.0046; *4*) 0.0057; *5*) 0.0074; *6*) 0.0100.

It has been established for iron ions that during the reaction their valence state changes. If trivalent iron is introduced into the initial benzene solution in water, then divalent iron appears and accumulates in the reaction, and conversely. The oxidation in the presence of copper ions is accelerated when a copper plate is introduced into the reactor, metallic copper dissolving during the reaction, i.e. the appearance in the system of copper(I) ions at a certain rate (formed by the reaction $Cu^0 + Cu^{2+} \rightarrow 2Cu^+$) stimulates the oxidation process. There is no doubt that oxidation-reduction reactions with participation of lower- and higher-valence ions play an important role in the catalytic oxidation of benzene.

The kinetics of the oxidation of benzene in the presence of iron and copper ions are very similar[89,90]. As the concentration of benzene increases, the maximum reaction rate w_{max} passes through a maximum, and the maximum concentration of phenol $[PhOH]_{max}$ increases linearly. With increase in the partial pressure of oxygen, both $[PhOH]_{max}$ and w_{max} increase. As the concentration of the catalyst is raised, w_{max} passes through a maximum and $[PhOH]_{max}$ increases in the presence of Cu^{2+} ions. An increase of the concentration of hydrogen ions entails a decrease of the reaction rate. Anions such as F^-, Cl^-, Br^-, CH_3COO^-, and SO_4^{2-} lower both the rate of accumulation of phenol and $[PhOH]_{max}$. Hydrocarbons (cumene, cyclohexene) and alcohols (isopropyl alcohol, cyclohexanol), introduced in an amount of 2% of the initial benzene, retard the oxidation of benzene. The maximum yield of phenol relative to benzene consumed (57%) was obtained in an experiment performed under the following conditions: 200°C, 0.012 M Cu^{2+}, 5 ml of benzene per 100 ml of water, duration 2 h, and P_{O_2} = 17.5 atm. The extent of reaction was 66%.

The mechanism of the oxidation of benzene in this reaction proved to be closely related to the mechanism of the oxidation of phenol and to the valence changes. Therefore a detailed study was made[93] of the oxidation of phenol under conditions similar to those in the oxidation of benzene and also of the oxidation of iron(II) ions. It was found that at 200°C in aqueous solution phenol is oxidised in three different ways: by reaction with molecular oxygen, by reaction with iron(III) ions, and by reaction with free radicals ($HO^\cdot$ and $HO_2^\cdot$).

Molecular phenol and phenoxide ions react with oxygen:

$$PhOH + O_2 \xrightarrow{k_0'} PhO^\cdot + HO_2^\cdot , \qquad (0')$$

$$PhOH + H_2O \rightleftarrows PhO^- + H_3O^+ ,$$

$$PhO^- + O_2 \xrightarrow{k_0''} PhO^\cdot + O_2^{-\cdot} , \qquad (0'')$$

$$O_2^{-\cdot} + H^+ \rightleftarrows HO_2^\cdot ,$$

$$PhOH + HO_2^\cdot \rightarrow PhO^\cdot + H_2O_2 ,$$

$$PhO^\cdot + O_2(HO_2^\cdot) \rightarrow \text{products of further oxidation}$$

(K_0 is the equilibrium constant).

It has been established experimentally that at 200°C $w = 2k[PhOH][O_2]$, $2k = a + b[H^+]^{-1}$, $a = (1.13 \pm 0.17) \times 10^{-5}$ litre mole^{-1} s^{-1}, and $b = (2.9 \pm 0.3) \times 10^{-6}$ s^{-1}. Comparison with the mechanism yields $\frac{1}{2}a = k_{0'}$ and $\frac{1}{2}b = K_0 k_{0''}$.

The reaction between phenol and Fe^{3+} ions was investigated under pressure in an atmosphere of argon. It was established that the reaction rate $w = k[PhOH][Fe^{3+}][H^+]^{-1}$ and $k = (3.5 \pm 0.2) \times 10^{-4}$ s^{-1} at 200°C.

It is suggested that the oxidation takes place according to the reaction

$$PhO^- + Fe^{3+} \rightarrow Fe^{2+} + PhO^\cdot \xrightarrow{Fe^{3+}} \text{molecular products.}$$

At 200°C Fe^{2+} ions (these were introduced in the form of Mohr's salt) are oxidised at the rate

$$w = (4.25 \cdot 10^{-3} + 9.0 \cdot 10^{-5}\,[H^+]^{-1})\,[Fe^{2+}]\,[O_2] \text{ mole litre}^{-1}\,\text{s}^{-1}.$$

According to the literature[95-103], the mechanism of the oxidation of Fe^{2+} ions is as follows

$$Fe^{2+} + O_2 \xrightarrow{k_2'} Fe^{3+} + O_2^- , \qquad (2')$$

$$Fe^{2+}\,aq \rightleftarrows FeOH^+ + H^+ ,$$

$$FeOH^+ + O_2 \xrightarrow{k_2''} FeOH^{2+} + O_2^- , \qquad (2'')$$

$$O_2^- + H^+ \rightleftarrows HO_2^\cdot ,$$

$$Fe^{2+} + HO_2^\cdot \rightarrow Fe^{3+} + HO_2^- ,$$

$$HO_2^- + H^+ \rightleftarrows H_2O_2 ,$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\cdot + OH^- ,$$

$$Fe^{2+} + HO^\cdot \rightarrow Fe^{3+} + OH^- .$$

Reactions (2′) and (2″) constitute the rate-limiting stage. Subsequent reactions with participation of $HO^\cdot$, HO_2, and H_2O_2 are very rapid and the concentrations of the reacting species (radicals and hydrogen peroxide) correspond to kinetic equilibrium. Since one oxygen molecule oxidises ultimately four Fe^{2+} ions, the rate of oxidation of Fe^{2+} according to the mechanism is $w = 4k_{2'}[Fe^{2+}][O_2] + 4k_{2''}K_2[Fe^{2+}][O_2][H^+]^{-1}$. Comparison with the experimental relations yields (for 200°C) $k_{2'} = 1.06 \times 10^{-3}$ litre mole^{-1} s^{-1} and $k_{2''}K_2 = 2.25 \times 10^{-5}$ s^{-1}. Sulphate ions accelerate the oxidation of Fe^{2+}.

The radicals $HO^\cdot$ and $HO_2^\cdot$, formed in the reactions of O_2 with Fe^{2+} and phenol, react with phenol. Therefore the mechanism for the oxidation of phenol can be represented by the following set of reactions (r$^\cdot$ is a general symbol for an active radical):

$$PhOH + O_2 \xrightarrow{k_0'} PhO^\cdot + HO_2^\cdot ,$$

$$PhO^- + O_2 \xrightarrow{k_0''} PhO + O_2^- ,$$

$$Fe^{2+} + O_2 \xrightarrow{k_2'} Fe^{3+} + r^\cdot ,$$

$$FeOH^+ + O_2 \xrightarrow{k_2''} FeOH^{2+} + r^\cdot ,$$

$$Fe^{2+} + r^\cdot \xrightarrow{k_3} Fe^{3+} + r^- ,$$

$$PhOH + r^\cdot \xrightarrow{k_4} PhO^\cdot + rH .$$

According to this mechanism, the rate of oxidation of phenol is

$$w = (k_0[O_2] + k_1[Fe^{3+}] + k_4[r^\cdot])[PhOH].$$

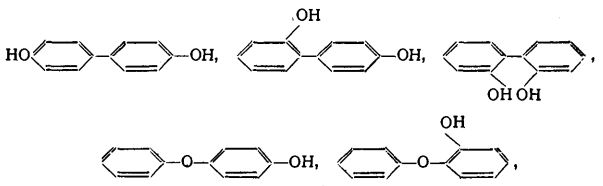
Table 3. Contribution of various reactions to the overall rate of oxidation of phenol at 200°C.

$[O_2]$, M	$[H^+]^{-1}$, litre mole^{-1}	$10^3[Fe^{3+}]$, M	$2 \times 10^5 k_0 \times [O_2]$, s^{-1}	$10^5 k_1 \times [Fe^{3+}]$, s^{-1}	$10^5 k_1 \times [r^\cdot]$, s^{-1}	$\frac{10^5 w}{[PhOH]}$, s^{-1}
0.22	12.6	2.2	1.05	0.97	0.73	2.75
0.22	12.6	1.1	1.05	0.48	0.47	2.00
0.22	12.6	0.5	1.05	0.22	0.03	1.30
0.22	12.0	0.9	0.88	0.38	0.50	1.76
0.44	6.0	17.0	1.20	4.10	5.70	11.00
0.22	52.4	0.2	3.00	0.36	0.81	4.17

Table 3 lists the rates of each of the three phenol consumption reactions for experiments with different initial conditions[93] and shows that the contribution of free-radical reactions ranges from 2 to 50% (in different experiments).

The reaction of hydroxy-radicals with phenol in aqueous solutions has been investigated[62,104-108]. Dixon and Norman[104] obtained hydroxy-radicals by the reaction of Ti^{3+} with hydrogen peroxide; in this system the formation of phenoxy-radicals from phenol was observed by the ESR method. It was reasonable to postulate the following reaction: $HO^\cdot + PhOH \rightarrow H_2O + PhO^\cdot$. However, it has been established by pulse radiolysis[62] that the primary radical product of the reaction of $HO^\cdot$ with phenol is dihydroxycyclohexadienyl, i.e. the hydroxy-radical adds to the phenol molecule: $HO^\cdot + C_6H_5OH \rightarrow HOC_6H_5\dot{O}H$. This contradiction has been resolved by Lamb and coworkers[105,106]. It was established by pulse radiolysis that the hydroxy-radical does indeed add to phenol but the $HOC_6H_5\dot{O}H$ radical formed is unstable and in aqueous solution is rapidly converted into the phenoxy-radical and water. The reaction is catalysed by H^+, OH^-, and $H_2PO_4^-$ ions. In aqueous solutions at pH 6.3 the rate constant for the decomposition of the radical[106] $HOC_6H_5\dot{O}H$ is 4.7×10^3 s^{-1}. This radical also reacts with other free radicals. The rate constant for the addition of $HO^\cdot$ to phenol in aqueous solution at room temperature is 1.06×10^{10} litre mole^{-1} s^{-1} at pH 6–7 [107] and 0.51×10^{10} at pH 9.[108]

In aqueous solutions phenoxy-radicals rapidly recombine with the ultimate formation of dimeric products. The recombination takes place with a rate constant $k = 5.6 \times 10^9$ litre mole^{-1} s^{-1} (determined by flash photolysis[109]). The following compounds have been observed among the products of the reaction of phenol in photolysis both in the presence and absence of oxygen[110]:



as well as dihydric phenols.

Thus kinetic data for the oxidation of phenol and modern ideas on the mechanism of the oxidation of Fe^{2+} show that in the catalytic oxidation of benzene in the presence of Fe^{2+} and Cu^{2+} ions benzene may be attacked by $HO^\cdot$ and $HO_2^\cdot$ radicals. At the initial point of the catalytic oxidation of benzene free radicals are formed by the reactions

$$Fe^{2+}aq + O_2 \rightarrow Fe^{3+}aq + O_2^- , \qquad (2')$$

$$Fe^{3+} + HO^- \rightarrow Fe^{2+} + HO^\cdot . \qquad (2'')$$

Reaction (2′) is much faster than reaction (2″) and therefore, on introduction of Fe^{2+} at the beginning of the reaction, the oxidation develops more rapidly than in the presence of Fe^{3+} ions. For the same reason, a copper surface in the presence of Cu^{2+} ions accelerates the process: the Cu^+ ions formed at a constant rate by the reaction of Cu^{2+} ions with metallic copper are then oxidised by O_2 with formation of O_2^- [by a reaction analogous to reaction (2′)]. Thus Fe^{2+} and Fe^{3+} ions (or Cu^{2+} and Cu^+) constitute the only source of $HO^\cdot$ and $HO_2^\cdot$ radicals at the beginning of the oxidation.

At an advanced stage of the reaction phenol begins to play a significant role in the formation of radicals. In the first place it reacts directly with O_2 forming O_2^-, which is then converted by a series of consecutive reactions into a hydroxyl radical:

$$O_2^- \overset{H^+}{\rightleftarrows} HO_2^\cdot \xrightarrow{Fe^{2+}} HO_2^- \overset{H^+}{\rightleftarrows} H_2O_2 \xrightarrow{Fe^{2+}} HO^\cdot .$$

In the second place, by reducing Fe^{3+} to Fe^{2+}, phenol increases the concentration of the latter and thus increases the rate of formation of radicals by reaction (2′). The increase in the rate of formation of radicals as phenol accumulates is in fact the reason for the autocatalytic course of the reaction.

The oxidation of benzene can be represented schematically by the following reactions:

$$\left.\begin{aligned} PhOH + O_2 &\xrightarrow{k_{0'}} PhO^{\cdot} + HO_2^{\cdot} \\ PhO^- + O_2 &\xrightarrow{k_{0''}} PhO^{\cdot} + O_2^- \\ Fe^{2+} + O_2 &\xrightarrow{k_{2'}} Fe^{3+} + O_2^- \\ FeOH^+ + O_2 &\xrightarrow{k_{2''}} FeOH^{2+} + O_2^- \end{aligned}\right\} \text{formation of free radicals}$$

$$\left.\begin{aligned} PhOH + r^{\cdot} &\xrightarrow{k_4} PhO^{\cdot} + rH \\ PhO^- + Fe^{3+} &\xrightarrow{k_5} PhO^{\cdot} + Fe^{2+} \end{aligned}\right\} \text{consumption of phenol}$$

$$C_6H_6 + r^{\cdot} \xrightarrow{k_6} PhOH \quad \text{formation of phenol.}$$

The present authors calculated[94] kinetic curves for the accumulation of phenol and consumption of benzene by this mechanism. The rate constants for reactions (0), (1), and (2) taken from experiments on the oxidation of phenol were used in the calculations and the ratio k_4/k_5 was evaluated from the ratio of the concentrations of benzene and phenol at the point corresponding to the maximum concentration of the latter, and the concentrations of Fe^{2+} and Fe^{3+} were determined experimentally. Under the experimental conditions (200°C, pH 1.90), the constants have the following values:

$$k_0 = k_{0'} + k_{0''}K_0[H^+]^{-1} = (2.43 \pm 0.30),\ 10^{-4} \text{ litre mole s}^{-1},$$
$$k_1 = (k_{1'}K_0 + k_{1''}K_1)[H^+]^{-1} = (2.80 \pm 0.20),\ 10^{-2} \text{ litre mole s}^{-1},$$
$$k_2 = k_{2'} + k_{2''}K_2[H^+]^{-1} = (2.86 \pm 0.20),\ 10^{-3} \text{ litre mole s}^{-1}.$$

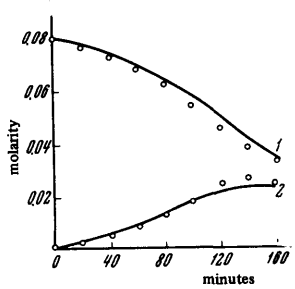


Figure 5. Experimental (circles) and calculated (lines) kinetic curves for the consumption of benzene (curve *1*) and accumulation of phenol (curve *2*).

Fig. 5 shows that the results of the calculations are in good agreement with experiment. The variation of the contribution of each reaction to the overall process of radical formation is plotted in Fig. 6. It is clearly seen that at an advanced stage the main source of radicals in the process is the reaction of phenol with oxygen.

The hydroxylation of benzene in this reaction takes place as a result of the addition of the radical to the benzene molecule. This is indicated by the closeness to unity of the isotope effect in the oxidation of C_6H_6 and C_6D_6 (k_H/k_D = 1.2) [78] and also the fact that the ratio of the rate constants for the reactions of radicals with benzene and phenol is close to unity[94]. Indeed if the free radical ($HO^{\cdot}$ or $HO_2^{\cdot}$) removed a hydrogen atom from benzene, then we should have $k_5 \ll k_4$, since the C–H bond energy in benzene is 102 kcal mole^{-1}, while the O–H bond energy in phenol is 85 kcal mole^{-1}. The available experimental data are so far insufficient for an estimate of the contribution of each radical ($HO^{\cdot}$ and $HO_2^{\cdot}$) to the hydroxylation of benzene.

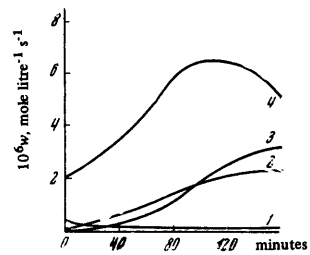


Figure 6. Rates of different reactions at 200°C, pH 1.90, and an oxygen pressure of 35 atm:
1) oxidation of Fe^{2+} ions; *2*) oxidation of phenol by oxygen; *3*) oxidation of phenol by reaction with radicals; *4*) consumption of benzene.

There is no doubt, however, that hydroxy-radicals hydroxylate benzene very vigorously, since it is known that at room temperature $k_{(HO^{\cdot}+C_6H_6)} = 4.3 \times 10^9$ litre mole^{-1} s^{-1},[45] i.e. the rate constant is very high. The question of the activity of the $HO_2^{\cdot}$ radical as a hydroxylating agent still remains obscure. Altogether, it has been shown that the catalytic oxidation of benzene in aqueous solution at 170–220°C is a coupled autocatalytic ion—radical reaction oxidising benzene and phenol by short chains, in which benzene is oxidised by radical addition; this in fact ensures a comparatively high yield of phenol. The chain length under the experimental conditions quoted in Fig. 5 is four units. Chain growth probably takes place by the reactions

$$C_6H_6 + HO^{\cdot} \rightarrow C_6H_7O^{\cdot},$$
$$C_6H_7O^{\cdot} + O_2 \rightarrow C_6H_5OH + HO_2^{\cdot},$$
$$HO_2^{\cdot} \xrightarrow{Fe^{2+}} HO_2^- \xrightarrow{H^+} H_2O_2 \xrightarrow{Fe^{2+}} HO^{\cdot}.$$

The benzene oxidation mechanism described above explains all the kinetic features of this reaction. The inhibiting effect of anions such as Cl^- and Br^- is due to the reactions

$$HO^{\cdot} + Cl^- \rightarrow HO^- + Cl^{\cdot},$$
$$Cl^{\cdot} + C_6H_5OH \rightarrow HCl + C_6H_5O^{\cdot}.$$

which lower the concentration of the hydroxylating agent, while phenol continues to disappear by reactions with $Cl^{\cdot}$ (or $Br^{\cdot}$). The inhibiting effect of certain organic additives[91] is also due to the fact that hydroxy-radicals are consumed in the oxidation of the organic compound and not in the hydroxylation of benzene.

VII. OTHER METHODS FOR THE OXIDATION OF BENZENE

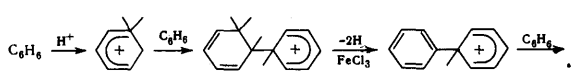
In a number of studies benzene was oxidised under pressure in liquid hydrofluoric acid[111-113]. The reaction at 200°C yields phenol, biphenyl, and carbon black, i.e. under these conditions oxidation is accompanied by dehydrogenation of benzene to carbon. Arsenic and selenium oxides make it possible to lower the oxidation temperature. The mixture hydrogen fluoride–boron trifluoride has also been employed as a catalyst[112], and O_2, ozone, sulphur dioxide, and atomic oxygen have served as oxidants. Phenol is formed in very small amounts.

Benzene can be oxidised to phenol using cupric sulphate as the oxidant by heating a mixture of benzene and aqueous cupric sulphate to 304°C.[114] The maximum yield of phenol (66%) is obtained when sodium phosphate is introduced together with cupric phosphate. Benzene can be oxidised to phenol with cupric acetate and benzoate (210–250°C, water)[115]. At 250°C 0.135 mole of phenol is formed in 5 h per mole of cupric sulphate consumed (benzene : water = 1 : 1). Phenol is obtained in the oxidation of benzene with oxygen at 300°C in the presence of water and the heterogeneous catalyst[116] 6% Cu–17% Mo on alumina. A high yield (75% relative to unreacted benzene) of phenol is obtained when benzene is oxidised with oxygen in benzoic acid in the presence of catalysts such as iron, copper, and silver oxides (260°C, water removed continuously by azeotropic distillation)[117].

The attempt to oxidise benzene in a hydrocarbon medium in the presence of suspended titanium salts and oxides at 25–100°C showed that under these conditions phenol is formed in negligible amounts[118].

Benzene can be polymerised to polyphenyl in the presence of Lewis acids, an oxidant, and water. When benzene is refluxed with anhydrous ferric chloride, a polyphenyl resin is formed[119]. Traces of water accelerate the reaction. Chlorobenzene is produced together with the polymer. Ferric chloride behaves as a catalyst of cationic polymerisation and as an oxidant:

$$H_2O + FeCl_3 \rightleftharpoons H^+ + Fe(OH)Cl_2,$$



A similar mechanism for the formation of polyphenyl from benzene has been suggested for the process in the presence of $MoCl_5$ and water[120] and in the presence of aluminium chloride, cupric chloride, and water. The polymer produced, parapolyphenyl, is thermally stable (up to 525°C) and has a high molecular weight.

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Valence Isomers of Benzene

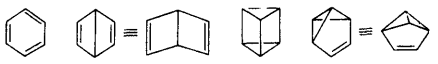
I.G.Bolesov

CONTENTS

I. Introduction 666
II. Methods of preparation of valence isomers of benzene 666
III. Properties of valence isomers of benzene 668

I. INTRODUCTION

Throughout the existence of the theory of the structure of organic compounds, probably no one structure attracted so much attention as that of benzene. As experimental data accumulated, the requirements which had to be met by the formula of benzene were defined. It must reflect (1) the high symmetry of the molecule (sixfold axis), (2) its planar structure, (3) the equivalence of all the hydrogen atoms, and (4) the unsaturated nature of the benzene molecule. One of the first benzene formulae (I) was proposed by Kekulé in 1865. This method of representation came to be generally accepted, although it does not take into account all the experimental data. An enormous variety of structures have been proposed as alternatives to the Kekulé formula (for a detailed discussion of this problem, see Menshutkin[1]). Among these the structures proposed by Dewar (II), Ladenburg (III) (prismane), and Hückel (IV) (benzvalene) should be mentioned.



(I) (II) (III) (IV)

For a long time it was believed that these structures not only cannot describe the properties of benzene but are in fact incapable of existence as non-planar valence isomers of benzene. Recently interest was aroused again in the "non-Kekulé" structures (II)–(IV). This is because in many cases, especially in photochemical reactions, it is difficult to account for the behaviour of aromatic compounds without postulating the intermediate formation of structures of the type (II)–(IV). Furthermore, the advances which have been already achieved in the chemistry of valence isomers of benzene have been attracting an increasing number of investigators.

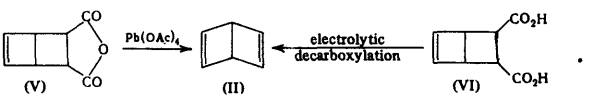
This review presents the main results of studies in the chemistry of this new and unusual field.

The reviews published hitherto on the chemistry of valence isomers of benzene deal with the literature up to the middle of 1965 [2,3] and those on the chemistry of Dewar hexamethylbenzene deal with the literature up to the middle of 1967.[4]

II. METHODS OF PREPARATION OF VALENCE ISOMERS OF BENZENE

1. From Bicyclo[2,2,0]hex-5-ene-2,3-dicarboxylic acid or Its Anhydride

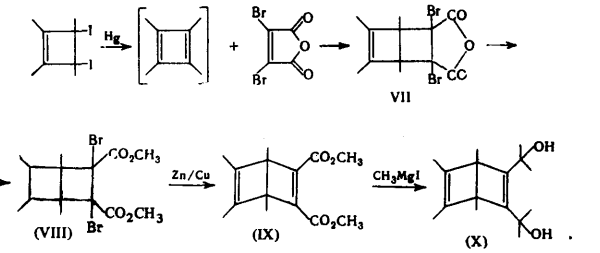
The first valence isomer of benzene, Dewar benzene (II), was obtained in 1963 by oxidising the anhydride (V) with lead tetra-acetate[5]. The yield of compound (II) was about 20%. Later a method of synthesis of compound (II) more convenient for preparative purposes was found—electrolytic decarboxylation of the acid (VI):[6]



(V) (II) (VI)

2. From Cyclobutadiene Generated *in situ*

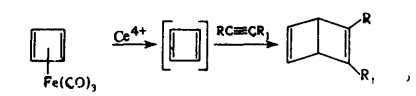
In order to obtain derivatives of Dewar benzene with different functional groups, it is necessary to carry out the condensation of tetramethylcyclobutadiene, obtained from 3,4-di-iodo-1,2,3,4-tetramethylcyclobut-1-ene, with dibromomaleic anhydride. The resulting anhydride (VII) is then further converted into the diester (VIII) and the latter is debrominated to form the "ester of Dewar phthalic acid" (IX):[7,8]



VII (VIII) (IX) (X)

Compound (IX) readily reacts with methylmagnesium iodide, forming a derivative of Dewar benzene (X).[9,10]

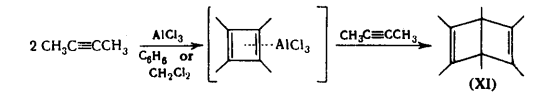
Cyclobutadienyliron tricarbonyl proved to be a convenient source of cyclobutadiene, adding readily to various acetylenes[11,12]:



where R = H and $R_1 = CO_2CH_3$, R = $R_1 = CO_2CH_3$, or R = H and $R_1 = C_6H_5$.

3. Trimerisation of Acetylene Derivatives

Preparatively the most simple synthesis of derivatives of Dewar benzene is that of hexamethylbicyclo[2,2,0]hexa-2,5-diene (XI), which consists in the trimerisation of but-2-yne under the action of aluminium chloride[4,13]:

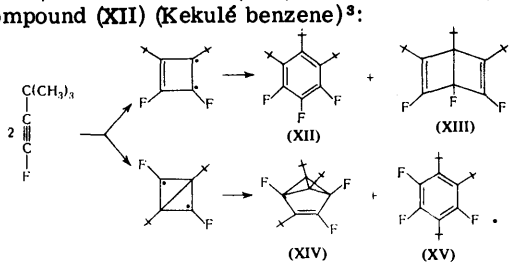


(XI)

Apart from aluminium chloride, aluminium bromide and $RAlCl_2$ (R = C_2H_5, C_3H_7, s-C_4H_9, or n-C_6H_{13}) can be used

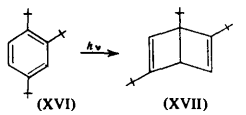
as catalysts. Other Lewis acids ($FeCl_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$, BF_3) and dialkylaluminium chlorides do not catalyst this reaction.

t-Butylfluoroacetylene forms very readily a mixture of trimers from which derivatives of bicyclo[2,2,0]hexa-2,5-diene (XIII) and benzvalene (XIV) were isolated together with compound (XII) (Kekulé benzene)[3]:

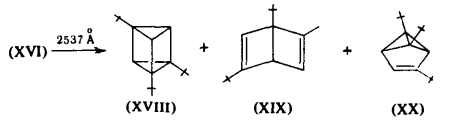


4. Photochemical Reactions of Benzene and Its Derivatives

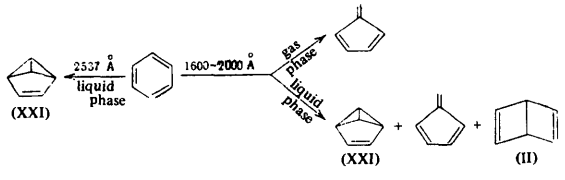
a. Valence isomerisation reactions. In 1962 it was shown that, on irradiation with ultraviolet light, 1,2,3,4-tri-t-butylbenzene (XVI) forms 1,2,5-tri-t-butylbicyclo[2,2,0]hexa-2,5-diene (XVII), a stable substance which can be purified by preparative chromatography on silica gel[14]:



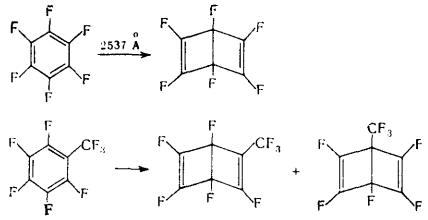
A detailed study of the photoisomerisation of polyalkylbenzenes showed that the observed migrations of alkyl groups are intramolecular processes accompanied by the rearrangement of the aromatic ring into prismane, benzvalene, and bicyclo[2,2,0]hexadiene derivatives, with subsequent rearomatisation[15-18]. Later it was established that, on irradiation with ultraviolet light at a wavelength of 2537 Å, corresponding to the second absorption maximum in the benzene spectrum, 1,2,4- and 1,3,5-tri-t-butylbenzene form a mixture of compounds (XVIII)–(XX), in which the principal component is prismane (XVIII)[18]:



Finally in 1967 it proved possible to synthesize the second (after Dewar benzene) valence isomer of benzene—benzovalene (XXI), characterised by PMR spectra and converted by methanolysis into familiar bicyclohexenyl ethers[19]. This reaction occurred on liquid-phase irradiation of benzene with ultraviolet light at a wavelength of 2537 Å. It is interesting to note that the irradiation of benzene in the gas phase at a wavelength of 1600–2000 Å results mainly in the formation of fulvene[20,21], while liquid-phase photolysis yields benzvalene, fulvene, and Dewar benzene in proportions of 5 : 2 : 1.[22]

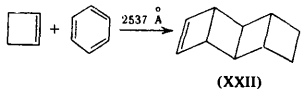


Gas-phase photolysis of hexafluorobenzene or octafluorotoluene results in the formation of the corresponding derivatives of Dewar's benzene,

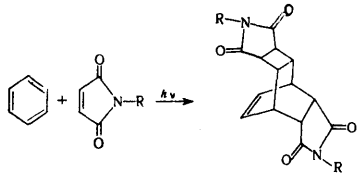


while in liquid-phase photolysis (in cyclohexane, methylcyclohexane, cyclo-octane, and ether) a complex mixture of products is formed[23-25].

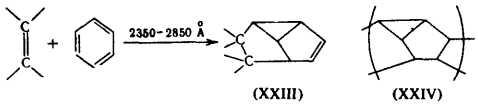
b. Reactions with olefins and dienes. When a 20% solution of cyclobutene in benzene was irradiated, the product isolated was a 1 : 1 adduct to which the structure (XXII) was ascribed[26]:



The imide of maleic acid and its *N*-alkyl, arylalkyl, and *N*-(*o*-tolyl) derivatives form 2 : 1 adducts with benzene, whose structure has been confirmed by synthesis[27]:

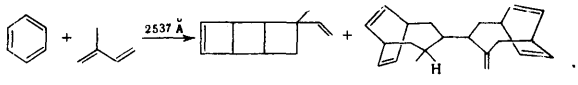


Various olefins (alkenes and cycloalkenes), unconjugated dienes, and ethyl vinyl ether form adducts with benzene as a result of 1,3-cycloaddition[28,29]:

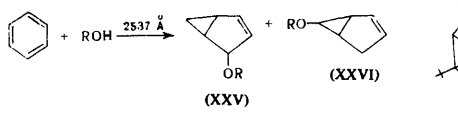


Such addition is accelerated in the presence of β-propiolactone; acetone and benzophenone do not affect the reaction rate[29]. Up to 85% of the adduct (XXIII) is obtained from cyclo-octene. Compounds of type (XXIII), like all other mono-olefins, also add to benzene, which can result in the formation of polymers to which the structure (XXIV) was ascribed (*n* reaches 24).[30]

Isoprene interacts with benzene, toluene, and tetra- and hexafluorobenzene by 1,2- and 1,4-cyclo-addition:[31]



c. Reactions with alcohols and acids. In the presence of methanol, trifluoroethanol, and acetic and phosphoric acids, benzene and 1,3,5-tri-t-butylbenzene form derivatives of bicyclo[3,1,0]hex-2-ene (XXV) and (XXVI):[32-34]



It is interesting to note that compound (XXVII) proves to be the sole product of the reaction of 1,3,5-tri-t-butylbenzene with methanol[34].

The mechanism of the above photoreactions of benzene has not been elucidated, but it has been suggested that these reactions proceed via singlet ($^1B_{2u}$) and triplet ($^3B_{1u}$) states of benzene[35] or via a reactive intermediate (with a Möbius type structure), which differ from the familiar excited states of benzene[36].

III. PROPERTIES OF VALENCE ISOMERS OF BENZENE

The reactivity of valence isomers of benzene has been investigated very little. The only exception in this respect are derivatives of Dewar benzene (especially hexamethylbicyclo[2,2,0]hexa-2,5-diene).

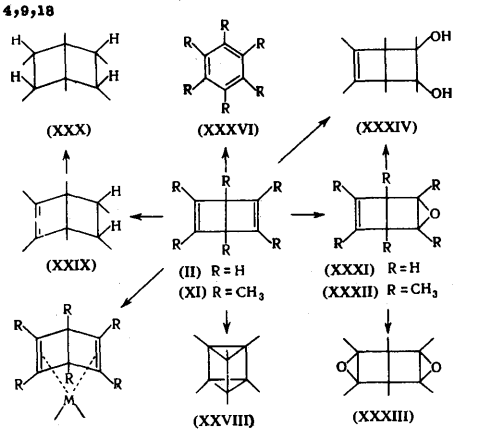
The stability of almost all the valence isomers of benzene examined above is quite sufficient under normal conditions for their isolation and purification.

1. Bicyclo[2,2,0]hexa-2,5-dienes

The PMR spectra of compounds (II) and (XI) show signals due to two types of protons: with $\tau = 3.45$ and 6.16 in the first case[5] and $\tau = 8.45$ and 8.95 in the second[4], the area ratios of the signals being 2 : 1. The first member of the series of Dewar benzenes—bicyclo[2,2,0]hexa-2,5-diene (II)—isomerises to benzene fairly readily even at 20°C (the period required for 50% conversion is about two days) and very rapidly at 90°C, but remains unchanged for a long time at 0°C in pyridine solution[5]. In contrast to bicyclo[2,2,0]hexa-2,5-dienes (II), the hexamethyl derivative (XI) rapidly isomerises to hexamethylbenzene only at about 150°C: the period of its 50% conversion to hexamethylbenzene is 105 h at 120°C, 5.5 h at 140°C, and 2.1 h at 150°C. The hexamethyl derivative of Dewar benzene has the following constants: b.p. 60°C (at 20 mmHg), m.p. 7.5°C, $n_D^{20} = 1.4479$, and $d_4^{20} = 0.8125$.[4]

Other bicyclo[2,2,0]hexadienes also isomerised to benzene derivatives on heating (in some cases only at 200°C)[4,9-12,14,24,37], under the action of Lewis acids[4], and in the presence of rhodium complexes of olefins[37]. Hexafluorobicyclo[2,2,0]hexa-2,5-diene is stable in the crystalline state but can explode in the liquid phase[24].

Under the action of ultraviolet light, bicyclo[2,2,0]-hexa-2,5-dienes are converted into prismane derivatives (XXVIII):[4,9,18]

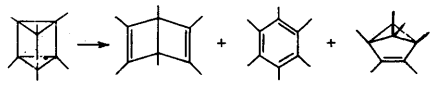


Hexamethylbicyclo[2,2,0]hexa-2,5-diene combines with hydrogen in the presence of catalysts and is reduced with carbodi-imide, forming dihydro-derivatives (XXIX) and tetrahydro-derivatives (XXX)[4,38]. Per-acids oxidise one or both olefinic groups of bicyclo[2,2,0]hexa-2,5-dienes (II) and (XI)[4,6]. Compound (XI) very readily oxidises in air to the diol (XXXIV), which is also obtained in the acid hydrolysis of the epoxide (XXXII)[4]. Treatment of bicyclo-[2,2,0]hexa-2,5-diene (II) with osmium tetroxide yields bicyclo[2,2,0]hexane-2,3,5,6-tetraol[6]. Dewar benzene and its hexamethyl derivatives form complexes with transition metals of type (XXXV)[6,37,39-41]. Other properties which deserve mention are the capacity of bicyclo[2,2,0]-hexa-2,5-dienes to combine with bromine with retention of the bicyclic structure[6,24], to undergo ozonolysis at one or two C=C bonds[4,9], and to exchange fluorine for an alkoxy-residue[24].

2. Prismanes

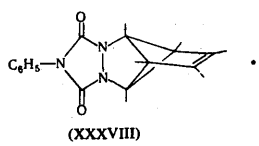
Hexamethylprismane (XXVIII), purified by repeated sublimation, melts at 89–90.5°C; its ultraviolet spectrum shows only terminal absorption characteristic of saturated hydrocarbons and the PMR spectrum has only a sharp singlet with $\delta = 0.97 \times 10^{-6}$.

Like bicyclo[2,2,0]hexa-2,5-dienes, prismanes are unstable at elevated temperatures. Under these conditions, they isomerise into derivatives of Kekulé and Dewar benzene[4,6,18,42]. At 129°C hexamethylprismane is converted to the extent of one third over a period of 30 min into a mixture of compounds (XI) and (XXXVI) in proportions of 2.4 : 1:



Lindlar's catalyst isomerises compound (XXVIII) into compounds (XI) and (XXXVI) and hexamethylbenzvalene (XXXVII). Boron trifluoride-ether causes instant isomerisation of compound (XXVIII) into a mixture of compounds (XI) and (XXXVI)[43]. It has been found that the ratio of compounds (XI) and (XXXVI) varies in the isomerisation of compound (XXVIII) by (a) heat treatment, (b) in the presence of $HF-BF_3$, and (c) in the presence of the rhodium complex of the hexamethyl derivative of Dewar benzene[42]. It has been found that the ratio (XI): (XXXVI) changes markedly under these conditions—from 1 : 30 in case (a) to 1 : 0.05 in case (c).

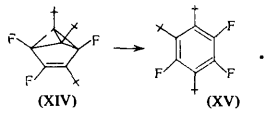
At 20°C hexamethylprismane readily forms adducts with 4-phenyltriazoline-3,5-dione and tetracyanoethylene, the structure (XXXVIII) being adopted for the first adduct[43]:



3. Benzvalenes

Benzvalene (IV), obtained by the liquid-phase photolysis of benzene (at 2537 Å), has a PMR spectrum with three resonance signals of equal intensities: an asymmetric triplet with $\tau = 4.05$, a symmetrical triplet with $\tau = 6.47$, and a quintet with $\tau = 8.16$. When acted upon by a methanol solution of hydrochloric acid, benzvalene (IV) is converted into known bicyclohexenyl ethers[19]. On heating,

1,3,6-tri-t-butyl-tricyclo[3,1,0,$0^{2,6}$]hex-3-ene (XX) isomerises exclusively to 1,2,4-tri-t-butylbenzene[18]. Similarly in the isomerisation of compound (XIV) the sole product is (XV):[3]



(XIV) (XV)

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During the preparation of the review for the press, the following new data on the chemistry of valence isomers of benzene were published.

Electrophilic addition of hydrogen halides (HCl and HBr) and methanol to Dewar hexamethylbenzene (XI), readily available from but-2-yne[4,13], leads to 1,2,3,4,5-pentamethyl-5-(α-X-ethyl)cyclopenta-1,3-dienes (X = Cl, Br, or CH_3O), isolated in yields of 45–85%.[44] To account for this course of reaction, a mechanism has been proposed postulating attack by a proton on the double bond with simultaneous or subsequent migration of the central bond, and stabilisation of the homoallyl cation by the nucleophilic agent X^-. The addition of chlorosulphonyl isocyanate to compound (XI) takes place similarly, the intermediate dipolar ion being stabilised intramolecularly with formation of an azasemifulvalene system[45].

When a methylene group is introduced into compound (XI) by treatment with diazomethane in the presence of cuprous bromide, a mixture of substances is formed[46]. The yield of products and the extent of conversion into cyclopropane derivatives strongly depends on the (XI) to CH_2N_2 ratio.

New data have been obtained on the reaction between compound (XI) and $RhCl_3.3H_2O$. The dark red crystalline compound formed has been assigned the structure of the dimer of pentamethylcyclopentadienylrhodium(III) chloride (XXXIX)[47] and not hexamethylbenzenerhodium(III) chloride, as stated earlier[41]. On being acted upon by triphenylphosphine, pyridine, or *p*-toluidine, compound (XXXIX) is converted into the monomeric adducts $[C_5(CH_3)_5]RhCl_2L$ (XL) (where L = triphenylphosphine, pyridine, or *p*-toluidine), while the reaction with cyclo-octa-1,5-diene in the presence of sodium carbonate yields (π-cyclo-octa-1,5-diene)(π-pentamethylcyclopentadienyl)-rhodium(I) (XLI). Elemental analysis, measurements of the molecular weight, and PMR spectra of compound (XXXIX) and the products (XL) and (XLI) obtained from it confirm the suggested structures. The mass spectrum of compound (XLI) contains intense peaks due to the molecular ion (m/e = 346) and the ion $[RhC_5(CH_3)_5]^+$ (m/e = 238).

Three types of reactions of hexafluorobenzene (XLII) with transition metal complexes have been described[48]: (1) like alkoxide ions[24], the anions $[Fe(CO)_2\pi\text{-}C_5H_5]^-$, $[Re(CO)_5]^-$, and $[Mn(CO)_5]^-$ substitute the vinyl fluorine atom; (2) manganese carbonyls with the general formula $RMn(CO)_5$ (R = H, CH_3, or C_6H_5) add to one multiple bond of compound (XLII); (3) tetrakis(triphenylphosphine)platinum forms a stable crystalline compound $Pt(C_6F_6)[P(C_6H_5)_3]_2$ (XLIII), the NMR spectrum of which contains three groups of signals of equal intensity (48.0×10^{-6}, 88.0×10^{-6}, and 99.8×10^{-6}), which have been ascribed to vinyl, Pt–C–F, and bridge fluorine nuclei. The infrared spectrum of compound (XLIII) contains a 1752 cm^{-1} band, but there is no absorption characteristic of a coordinated double bond. In view of this finding, it has been concluded that the molecule of compound (XLIII) contains a threemembered ring with C–Pt σ-bonds.

It has been shown that, in the vapour-phase photolysis (at 2537–2370 Å) of benzene, benzvalene (IV) is formed at very low concentrations[49]. The amount of compound (IV) increases when the photolysis is carried out in the presence of gases, whose efficiency varies in the following sequence: nitrogen < neopentane < *cis*-but-2-ene.

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Methods of Preparation and Properties of Compounds with Unsaturated Groups at the Phosphorus Atom

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The review deals with problems connected with the synthesis, chemical properties, and applications of organophosphorus compounds with unsaturated groups at the heteroatom. A systematic account is given of the methods of preparation of these substances and the characteristic features and limits of applicability of the synthetic methods, in accordance with the wide variety of structures of the products considered, are noted. The section dealing with the properties of the compounds describes the addition reactions of nucleophilic agents, reactions with substances with a tendency towards homolysis, certain rearrangements, condensations, and other processes. The practical value of compounds with unsaturated groups at the phosphorus atom is noted. The bibliography comprises 344 references.

CONTENTS

I. Introduction 670
II. Preparation of compounds with unsaturated groups at the phosphorus atom 670
III. Properties of compounds with unsaturated groups at the phosphorus atom 674

I. INTRODUCTION

The chemistry of organophosphorus compounds has developed considerably in recent years. A large number of substances of practical value have been synthesised and compounds with unsaturated groups at the phosphorus atom are of definite interest in view of the wide variety of their chemical properties. Non-combustible and self-extinguishing polymers, effective preparations with a wide variety of physiological activity, etc. have already been obtained on their basis.

At the present time there are no publications dealing with the main features of such investigations and the present review is an attempt to fill this gap. It deals with two topics, the methods of preparation of alkenylphosphorus compounds and their reactivity, the literature data published up to the middle of 1966 being discussed.

II. PREPARATION OF COMPOUNDS WITH UNSATURATED GROUPS AT THE PHOSPHORUS ATOM

Compounds of this type were synthesised about 50 years ago in the study of the reaction of phosphorus pentachloride with olefins, but the principal methods of their preparation have been developed only in the last 20 years.

1. Interaction of Halogeno-derivatives of Phosphorus with Metal Alkyls

This method of synthesis was quite recently developed and is used mainly for the preparation of phosphorus(III) compounds. In 1959 Kaesz and Stone[1] carried out the vinylation of phosphorus trichloride with divinylmercury[1]:

$$(CH_2{=}CH)_2Hg + PCl_3 \rightarrow CH_2{=}CHPCl_2 + CH_2{=}CHHgCl.$$

The yield of vinyldichlorophosphine was 50%; the compound proved to be very sensitive to air and moisture. Sterlin et al.[2] carried out a similar reaction with perfluorovinyl derivatives:

$$CF_2{=}CFMgX + PCl_3 \rightarrow (CF_2{=}CF)_3P.$$

Related methods have been proposed in Foster's[3,4] and Feder's[5] patents. In 1960 Leavitt and coworkers synthesised cyclic phosphorus compounds from dilithium derivatives and phenyldichlorophosphine[6,7]. Next one may refer to the work of Rabinowitz[8], Maier[9], and Zeiss[10] on further improvement of the method and the investigation of the properties of these compounds.

Kabachnik and Chang Jung-Yü[11,12] and Razumov[13] extended these reactions to dialkyl- and dialkoxy-chlorophosphines.

Double decomposition reactions of alkyl(aryl)magnesium halides with unsaturated phosphines are also possible [14]:

$$C_6H_5CH{=}CHPCl_2 + 2\ RMgHal \rightarrow C_6H_5CH{=}CHPR_2\ .$$

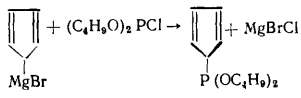
Similar reactions can be performed with metallic derivatives of acetylenes. For example, Chodkiewicz and coworkers studied the following reactions of alkynylmagnesium halides [15,16]:

$$RC{\equiv}CMgX^+ \left| \begin{array}{l} PCl_3 \rightarrow (RC{\equiv}C)_3P, \\ POCl_3 \rightarrow (RC{\equiv}C)_3P{=}O, \\ (C_6H_5)_2PCl \rightarrow (C_6H_5)_2PC{\equiv}CR\ . \end{array} \right.$$

Kabachnik and coworkers carried out similar reactions with dialkyl phosphorochloridites [17] and Maretina and Petrov with dialkylchlorophosphines [18]. The yield of alkyl derivatives was 50–70% [19–23]. Hartmann and coworkers [24,25] and Maler [26] carried out the interesting synthesis of acetylenic diphosphines:

$$2\ (C_6H_5)_2PCl + BrMgC{\equiv}CMgBr \xrightarrow{ether} (C_6H_5)_2PC{\equiv}CP(C_6H_5)_2 + MgCl_2 + MgBr_2\ .$$

Kabachnik and Tsvetkov established that the method can be used for the synthesis of phosphorus compounds with cyclic unsaturated groups, for example, derivatives of cyclopentadiene, indene, and fluorene [27–29]:



Instead of phosphorochloridites, in some cases the alkoxyderivatives can react with organomagnesium compounds [30]:

$$RR'POR'' + CH_2{=}CHMgX \rightarrow RR'PCH{=}CH_2 + MgX(OR)\ .$$

2. Interaction of Metal Derivatives of Phosphorus with Alkyl Halides

The second method of preparation of unsaturated phosphorus compounds is based on the reaction

$$MP^{III(V)} + R{-}Hal \rightarrow MHal + R{-}P^{III(V)}\ ,$$

where M is an alkali metal and Hal a halogen atom. The reactions of metal derivatives of phosphines with halogenoalkenes take place in an inert medium over a wide range of temperatures [31–33]:

$$C_6H_5PHNa + Br(CR')_nC{=}CH_2 \rightarrow C_6H_5PH(CR')_nCR{=}CH_2 + NaBr$$

An interesting process is dealkylation with a secondary phosphide ion, which leads to alkenylphosphines [34]:

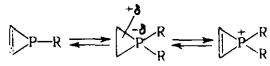
$$(C_6H_5)_2PH + C_4H_9Li \rightarrow (C_6H_5)_2P{-}Li + C_4H_{10}\ ,$$

$$C_6H_5OCH_2CH{=}CH_2 \xrightarrow{(C_6H_5)_2PLi} C_6H_5OLi + (C_6H_5)_2PCH_2CH{=}CH_2\ .$$

Lithium phosphides react with acetylenes [35,36] to form addition products:

$$R_2PLi + CH{\equiv}C{-}CH{=}CH_2 \rightarrow \left\{ \begin{array}{l} CH{\equiv}C{-}CH_2{-}CH_2{-}PR_2, \\ CH_2{=}C{=}CH{-}CH_2{-}PR_2, \\ CH_2{=}CH{-}CH{=}CH{-}PR_2\ . \end{array} \right.$$

Some investigators have discussed the possibility of the existence of three-membered structures with phosphorus as a heteroatom [37,38]:



and also other intermediate alkenyl derivatives of phosphorus [39]. The Michaelis–Bekker reaction is a variant of the above method preparation of organophosphorus compounds with unsaturated groups at the phosphorus atom. Alkenylphosphonates are formed in the reaction of alkenyl halides with alkali metal salts of dialkyl phosphorous aicds [40,41]:

$$R'CH{=}CHCH_2Cl + NaOP(OR)_2 \rightarrow R'CH{=}CHCH_2\overset{\overset{O}{\|}}{P}(OR)_2 + NaCl\ .$$

The Michaelis–Bekker method permits the synthesis of the same substances as the Arbuzov rearrangement, although it is not quite so universal because of the occurrence in many cases of side reactions, for example, the allyl rearrangement [42,43]. The yield of alkenylphosphonate esters in the Michaelis–Bekker reaction is usually lower than in the Arbuzov reaction. Nevertheless a wide variety of alkenylphosphonates have been obtained by this method: allyl- [44], butenyl- [45], butoxypentenyl- [43], cycloalkenyl- [46–48], and others [49–53]. The sodium salt of diethylphosphorothious acid can be used in this reaction instead of sodium diethyl phosphite [43,44]:

$$CH_2{=}CHCH_2Br + (RO_2)P{-}SNa \rightarrow CH_2{=}CHCH_2\overset{\overset{S}{\|}}{P}(OR)_2\ .$$

Diphosphono-derivatives, which are products of the subsequent condensation of dialkyl phosphites with the alkenylphosphonates formed, are almost absent in this case [54,55].

3. The Arbuzov Rearrangement

This most general method of synthesising organophosphorus compounds can be used also for the preparation of compounds with unsaturated groups at the phosphorus atom. The starting materials are either alkenyl halides or polyhalogenoalkanes; in the latter case the products of the rearrangement are dehydrohalogenated [56–59]:

$$CH_2{=}CHCH_2Hal + P(OR)_3 \rightarrow CH_2{=}CHCH_2\overset{\overset{O}{\|}}{P}(OR)_2 + RHal\ ,$$

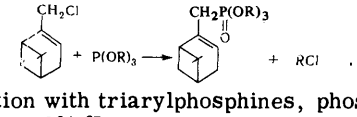
$$CH_3\underset{Br}{CH}{-}\underset{Br}{CH_2} + P(OR)_3 \xrightarrow[-RBr]{} CH_3CH{-}CH_2{-}\overset{\overset{O}{\|}}{P}(OR)_2 \xrightarrow[-HBr]{} CH_3CH{=}CH\overset{\overset{O}{\|}}{P}(OR)_2\ .$$

(Hal = Cl, Br)

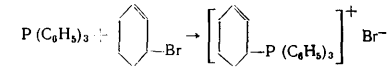
The rate of the process depends on a number of factors—temperature, proportions of the reactants, nature of the alkyl halide, and also the structure of the initial phosphorus(III) compound. Liorber and Razumov found that allylphosphonite esters undergo the Arbuzov rearrangement much more readily than alkyl- and vinyl-phosphonites. Thus, depending on the nature of the group joined to the phosphorus atom, phosphorus(III) compounds can be arranged in the following series [60]:

$$CH_2{=}CHCH_2P(OR)_2 > AlkP(OR)_2 > CH_2{=}CHP(OR)_2\ .$$

Certain more complex alkyl halides readily undergo the Arbuzov reaction [61–63]:

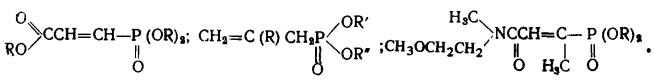


In the reaction with triarylphosphines, phosphonium halides are formed [64–67]:

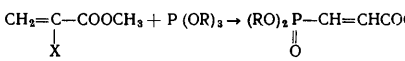


When α-halogeno-ketones are used as the initial alkyl halides, the rearrangement can be more profound [67–69].

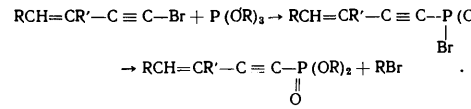
At the present time the Arbuzov rearrangement constitutes a widely used method for the synthesis of alkenylphosphonates, whereby it is possible to obtain very complex compounds, for example[70-74]:



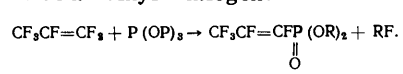
The reaction of trialkyl phosphites with α-halogenoacrylates is very interesting[75]:



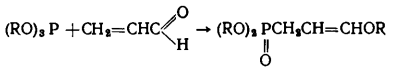
Ionin and Petrov found that halogenoacetylenes can also undergo the Arbuzov rearrangement[76,77]:



Such rearrangements take place particularly readily when the triple bond is conjugated with another multiple bond or a benzene ring[78,79]. Knuyants and coworkers showed that perfluoro-olefins can react with trialkyl phosphites[80-84], this being the first example of the Arbuzov rearrangement of compounds with a "vinyl" halogen:

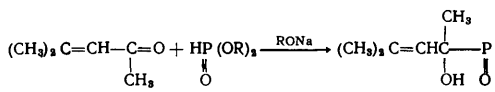


Trialkyl phosphites react by an Arbuzov rearrangement mechanism with $\alpha\beta$-unsaturated carbonyl compounds[85-88], the reaction being extremely specific:

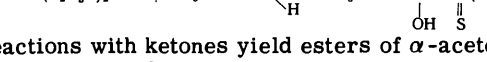


4. Addition Reactions of Dialkyl Phosphites

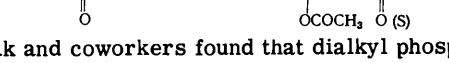
The methods of synthesis of alkenylphosphonates via various reactions of dialkyl phosphites are very unusual and as a rule comparatively simple. Thus Abramov, Pudovik et. al. found that dialkyl phosphites readily react with unsaturated carbonyl compounds forming derivatives of α-hydroxyallylphosphonic acid[89-93]:



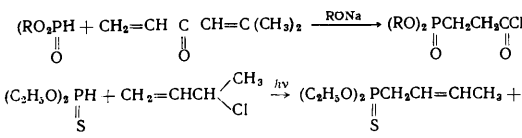
Dialkyl phosphorothi-ites react similarly[94]:



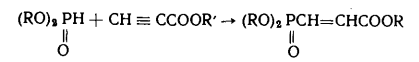
Reactions with ketones yield esters of α-acetoxyvinylphosphonic acid[95-97]:



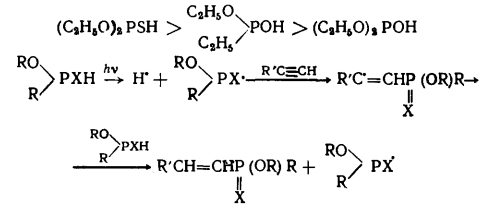
Pudovik and coworkers found that dialkyl phosphites readily add to certain $\alpha\beta$-unsaturated carbonyl compounds, yielding alkenylphosphonates[98-105]:



The yield of products is 50–70%. The reaction with propiolic acid derivatives gives β-alkoxycarbonylvinylphosphonates[106]:

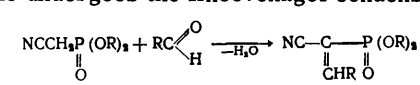


Pudovik and coworkers showed that the reaction of dialkyl phosphoric acids with certain acetylenes can involve a radical mechanism. The addition takes place contrary to the Markovnikov rule; the rate of the process decreases in the series[105]:

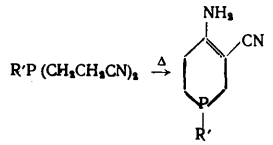


5. Certain Special Methods for the Preparation of Alkenylphosphonates

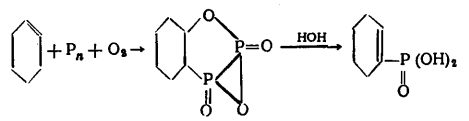
According to the data of Kirillov and Petrov, phosphonoacetonitrile undergoes the Knoevenagel condensation[107]:



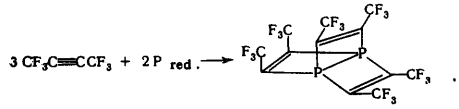
Alkylbis-(β-cyanoethyl)phosphines isomerise to phosphorins in boiling toluene[108-111]:



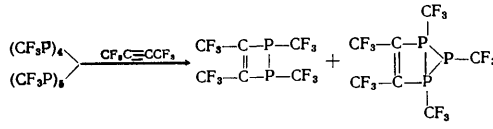
Certain cyclic alkenylphosphines can be obtained from elemental phosphorus[112-114]:



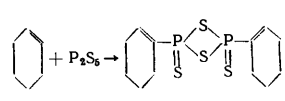
or[115,116]:



Similar polyphosphine heterocycles are formed in high yield when tetra and penta-trifluoromethylphosphines are heated with *sym*-hexafluorobutyne[117]:



Unusual alkenyl structures are produced in the reaction between phosphorus pentasulphide and olefins[118,119]:



6. Reactions Using Phosphorus Trichloride

Much work has been done on the study of the possibility of using phosphorus trichloride to synthesise compounds with a C–P bond, including alkenylphosphonates. Usually the second component is an olefin [120]:

$$PCl_3 + RCH{=}CH_2 \xrightarrow[H_2O]{(CH_3CO)_2O} RCH{=}CHP(O)(OH)_2 \quad .$$

Sometimes ketones are used in the reaction [121-125]:

$$C_6H_5CCH_3 + PCl_3 + CH_3COOH \xrightarrow{HOH;\ HCl} CH_2{=}C(C_6H_5){-}P(O)(OH)_2 \quad .$$

Kinnear, Perren, and other investigators have successfully employed in these processes the complex-forming capacity of aluminium chloride [126,127]:

$$RCl + PCl_3 + AlCl_3 \rightarrow RPCl_4 \cdot AlCl_3 \xrightarrow{HOH} RP(O)Cl_2 + HCl + Al(OH)_3 \quad ,$$

where R = alkenyl.

An extensive series of investigations by Soborovskii, Zinov'ev, and coworkers dealt with the oxidative chlorophosphination of hydrocarbons, including unsaturated hydrocarbons, which makes certain alkenylphosphonates extremely easy to obtain [128-134]:

$$CH_2{=}CHCl + PCl_3 + O_2 \rightarrow CH_2ClCHClP(O)Cl_2 \xrightarrow{ROH}$$

$$\rightarrow CH_2ClCHClP(O)(OR)_2 \xrightarrow{Zn} CH_2{=}CHP(O)(OR)_2 ,$$

$$RC{\equiv}CH + 2\,PCl_3 + O_2 \rightarrow RCCl{=}CHP(O)Cl_2 + POCl_3 \quad .$$

Recently a method has been found, and has been developed successfully, for the synthesis of alkenylphosphonates by the thermal (so called "pseudo-Claisen") rearrangement of various phosphite esters, primarily allyl and propargyl esters [135-140]:

$$(RO)_2P{-}OCH_2CH{=}CHCH_3 \xrightarrow{180^\circ} (RO)_2P(O){-}CHCH{=}CH_2 ,$$

$$(RO)_2P{-}OCH_2C{\equiv}CH \xrightarrow{180^\circ} (RO)_2PCH{=}C{=}CH_2 \rightarrow (RO)_2PC{\equiv}C{-}CH_3 \quad .$$

A possible mechanism of the isomerisation has been put forward [139,140].

7. Reactions of Phosphorus Pentachloride and Its Derivatives with Unsaturated Compounds

The most familiar and most thoroughly developed method for the synthesis of various compounds with alkenyl groups at the phosphorus atom is based on the interaction of phosphorus pentachloride with olefins. As early as 1894, Marsh and Gardner [141,142] stated that camphene reacts with phosphorus pentachloride to form a product which yields camphenylphosphonic acid after hydrolysis. Later, reactions of phosphorus pentachloride with styrene, isobutene, and other unsaturated hydrocarbons were described and it was found that the process takes place best with asymmetric polar systems; the PCl_4 group becomes attached to the most hydrogenated carbon atom and chlorine to the least hydrogenated carbon atom [143,144]. Bergmann and Bondi noted that at least a twofold excess of phosphorus pentachloride is necessary for satisfactory yields [145-147]:

$$RCH{=}CH_2 + 2\,PCl_5 \rightarrow RCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{HOH} RCH{=}CHP(O)(OH)_2 \quad .$$

It was found that the intermediate complexes can be treated with agents other than water under different conditions [148-150], namely phosphorus pentasulphide [151-152], sulphur [152-155], hydrogen sulphide [156-159], hydrogen selenide [160], and elemental phosphorus [151,158], or they can be heat-treated [151,159]. The yield of the acid chlorides of alkenylphosphonic acids and their analogous thio-derivatives is in the range 60–80%. The method was successfully extended to various styrene derivatives [148,161-163], diene hydrocarbons [164-166], and acetylenes [148,167-172].

It has been established that, depending on the structure of the initial diene and the reaction conditions, phosphorus pentachloride can add both in 1,2- [153,173] and 1,4-positions [174]. Anisimov, Nesmeyanov, Kolobova, and others employed extensively the reaction of phosphorus pentachloride with alkyl vinyl ethers [175-178] and alkyl vinyl sulphides [179,180]:

$$ROCH{=}CH_2 + 2\,PCl_5 \rightarrow ROCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{SO_2} ROCH{=}CHPCl_2(O) ,$$

$$RSCH{=}CH_2 + 2\,PCl_5 \rightarrow RSCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{SO_2} RSCH{=}CHPCl_2(O) \quad .$$

As can be seen from the above equations, it was found that the addition takes place in accordance with the Markovnikov rule [178-182]; cycloalkenyl ethers react similarly [183,184].

The treatment of the intermediate complexes with elemental phosphorus is now attracting increasing attention as a convenient method for the preparation of $\alpha\beta$-unsaturated phosphines [185,186]:

$$ROCH{=}CH_2 + 2\,PCl_5 \rightarrow ROCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{P} ROCH{=}CHPCl_2 \quad .$$

Lutsenko, Kirillov et al. found that the reaction of phosphorus pentachloride with enol esters leads to a wide variety of products. Various substituted alkenylphosphonates can be isolated [187-192]:

$$CH_3C(OCOCH_3){=}CH_2 + PCl_5 \rightarrow CH_3CCl(OCOCH_3)CH_2PCl_4 \xrightarrow{PCl_5,\ CH_3COCl,\ SO_2} CH_3CCl(COCH_3){=}C(O){-}PCl_2 \quad .$$

Apart from phosphorus pentachloride, other phosphorus(V) derivatives, primarily alkyl-and aryl-tetrachlorophosphoranes, can add to olefins [193-196]:

$$C_6H_5PCl_4 + CH_2{=}CHOC_2H_5 \rightarrow C_6H_5PCl_3CH_2CH(Cl)(OC_2H_5) \xrightarrow{SO_2} C_6H_5P(O)(Cl)(CH{=}CHOC_2H_5) \quad .$$

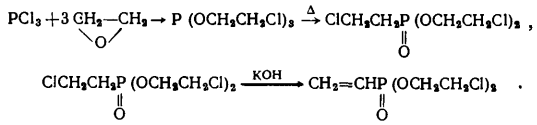
Recently it has been found that certain phosphorus(III) derivatives, mainly phosphorus trichloride [197,198] and tribromide [199-201], alkyl- and aryl-halogenophosphines [202,203], and alkyl and aryl phosphorochloridites [204-212], add readily to dienes, for example:

$$CH_2{=}CH{-}CH{=}CH_2 + ClP(O{-}CH_2{-}CH_2{-}O) \rightarrow \text{bicyclic adduct}(O{=}P{-}OCH_2CH_2Cl) \quad .$$

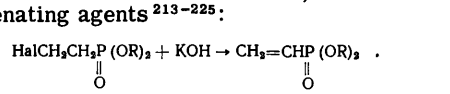
8. Elimination of Water and Acids from Saturated Organophosphorus Compounds

To conclude this review of synthetic methods for compounds with unsaturated groups at the phosphorus atom, we shall consider various methods for the elimination of the elements of water and acids from saturated organophosphorus compounds. Much attention has been devoted to this problem in the literature because various kinds of β-halogenophosphonates are at the present time some of the most widely available organophosphorus compounds and are obtained as a rule by the reaction of phosphorus halides

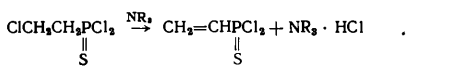
or their derivatives with epoxyalkanes followed by thermal isomerisation[213-218]:



A wide variety of basic substances, especially aqueous or aqueous-alcoholic solutions of alkalis, can be used as dehydrohalogenating agents[213-225]:

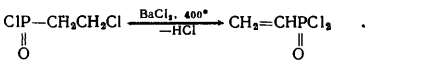


Tertiary amines and in particular triethylamine are dehydrohalogenating agents which come next in order of importance as regards frequency of application. In this case acid halides can also be introduced into the reaction[218,225]:

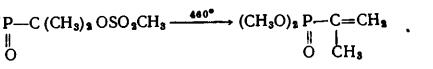


Alkali metal acetates[226-230], sodium carbonate[231], potassium t-butoxide[227], alkali metal hydrides[221], and activated charcoal[232-234] can be used as dehalogenating agents.

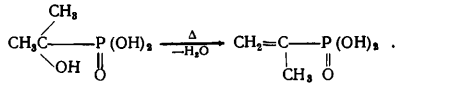
Thermal elimination of hydrogen halides, in the first place hydrogen chloride, is applicable to a comparatively narrow range of substances, but is technologically very promising and is now being effectively developed[235-241]:



The elimination of the elements of acids other than hydrogen halides takes place less completely and is frequently accompanied by side processes[97,242]:



Thermal degradation has been developed to an even lesser extent, although there are certain promising results showing that such a process is in principle possible[243,244]:



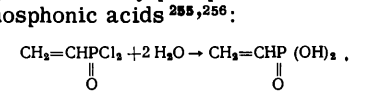
On the whole, the synthesis of organophosphorus structures with unsaturated groups at the heteroatom by the elimination of the elements of acids is at the present time most widely used both in the laboratory and in industrial practice[242,245-254].

III. PROPERTIES OF COMPOUNDS WITH UNSATURATED GROUPS AT THE PHOSPHORUS ATOM

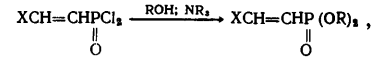
1. Reactions Not Involving the Multiple Bond

a. Synthesis of esters, thioesters, and amides. It is noteworthy that, whereas the methods of preparation of the compounds under consideration have been developed comparatively fully, their chemical properties have been investigated to a much lesser extent. Only the double-decomposition reactions of alkenylphosphonic halides, certain nucleophilic addition reactions, and the tendency towards polymerisation have been investigated. Oxidation and reduction processes and certain specific rearrangements and condensation have been studied to a very limited degree.

The hydrolysis of alkenylphosphonic halides yields unsaturated phosphonic acids[255,256]:

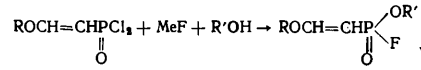


Esters of these acids are usually obtained from their chlorides and alcohols in an inert solvent; various tertiary amines are used as acceptors for hydrogen chloride[257-267]:

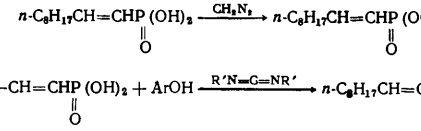


where X = H, alkyl, halogen, Sr, etc.

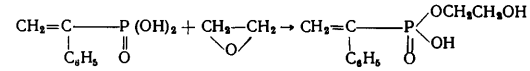
The yields of esters prepared in this way amount to 40-60%. Certain monoester acid fluorides can be obtained by acting upon the dichloride simultaneously with an alcohol and a metal fluoride[268]:



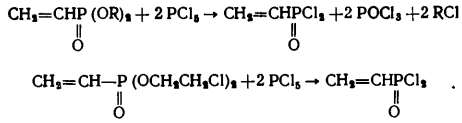
Higher unsaturated phosphonic acids can be esterified with diazomethane and also alcohols and phenols in the presence of carbodi-imide[269]:



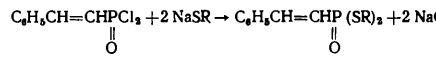
Ivin and coworkers showed that certain higher alkenylphosphonic acids react with epoxides to form mono-β-hydroxyalkyl esters[270]:



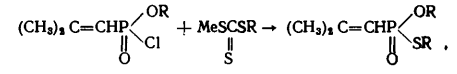
The reverse reaction – the interaction of alkenylphosphonates with phosphorus pentachloride–is possible[256,268]:



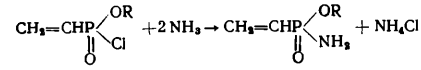
Thioesters of alkenylphosphonic acids [phosphonodithiolates (Translator)] are obtained in good yields when mercaptides react with the acid dichlorides[271-274]:



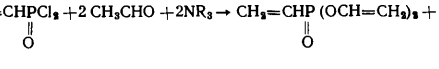
The reaction with salts of alkyltrithiocarbonic acid is similar[274]:



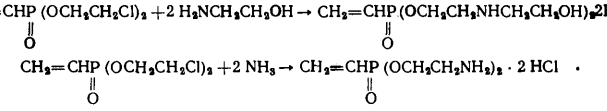
When the acid dichlorides react with ammonia and amines, the amides of alkenylphosphonic acids are formed[275-279]:



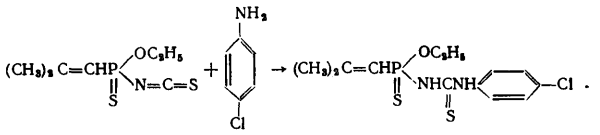
Gefter, Kabachnik, and coworkers extended the general method to alkenylphosphonates for the synthesis of vinyl esters[280,281]:



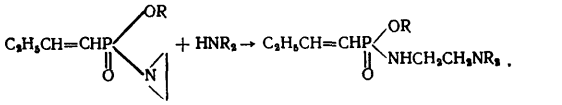
In the presence of halogen atoms in the saturated group, there is a possibility of their exchange for amino-groups, NR_2 groups, etc.[282]:



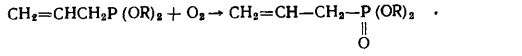
Alkenylphosphonyl thiocyanates enter into all the reactions characteristic of thiocyanates[283]:



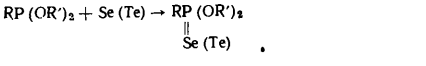
Ethyleneimides are fairly readily cleaved by compounds containing a mobile hydrogen atom[284]:



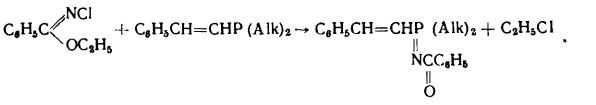
b. Oxidation and reduction reactions. Oxidation and reduction reactions of compounds with unsaturated groups at the phosphorus atom have been very little studied. Whereas the oxidation of various phosphorus(III) structures with oxygen, sulphur, selenium, and tellurium is known if only in principle, there have been almost no studies on reduction. The oxidation of phosphorus(III) compounds with oxygen has been most thoroughly investigated[8-13]. This process, which takes place very readily as a rule, begins sometimes when the substance simply comes into contact with atmospheric oxygen:



Sulphur, selenium, and tellurium add under much more severe conditions[12-16,19-22,285]:

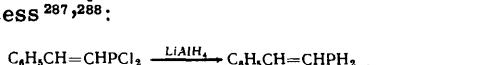


The reaction of tertiary unsaturated phosphines with chloroiminoethers must be classified as an oxidation reaction[286]:

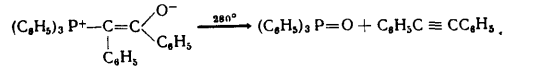


The oxidation of the compounds considered with ozone occupies a special place. As with ordinary olefins, this reaction causes a profound degradation of the molecule, which leads to carbonyl compounds or acids depending on the conditions[96,173].

Lithium aluminium hydride can be used as the reducing agent, since the multiple bond is then unaffected in the reduction process[287,288]:

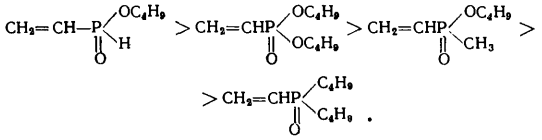


Pyrolysis of certain alkenylphosphonates results in the degradation of the molecule at the C – P bond[289]:



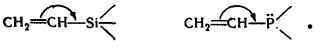
2. Reactions at the Multiple Bond

a. Nucleophilic addition. The specific features of alkenylphosphonates are shown in the study of various reactions involving the multiple bonds. The reviews of Kabachnik[290], Gefter[291], and Pudovik[54] have dealt with certain aspects of these interactions and their systematic description. The general properties of organophosphorus compounds with vinyl groups are described in Kabachnik's review and the problem of the conjugation of the multiple bond with trivalent and pentavalent phosphorus atoms is discussed. The author concludes that, although physicochemical methods such as infrared and ultraviolet spectroscopy and calculations of molar refractions fail to confirm the occurrence of conjugation, ESR data do indicate its existence. This is also shown by a whole series of chemical properties. For example addition reactions of various nucleophilic agents involving the double bond of organophosphorus compounds take place very readily, the proton always adding at the α-position with respect to the P=O group. Unsaturated organophosphorus compounds can be arranged in the following sequence in terms of decreasing capacity for such addition[292-294]:



The addition to the first member of the series takes place vigorously with evolution of much heat, while the addition to the last member requires prolonged heating. This is due to the increasing positive inductive effect of the substituents at the phosphorus atom. Therefore the addition of electrophilic agents should follow the opposite sequence—dibutylvinylphosphine oxide should be the most reactive.

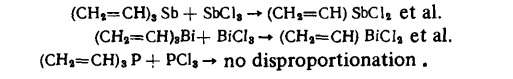
The addition of a nucleophilic group to phosphorus(III) compounds of the type $CH_2=CHPR_2$ also takes place at the β-position (although the inductive effect should lead to α-addition. Here evidently the participation of phosphorus d-orbitals in conjugation has an effect, as happens in vinylsilanes[295-297]:



In agreement with the above findings, dialkylamides of vinylphosphonic acid have lost almost completely the capacity to combine with nucleophilic agents, but readily combine with electrophilic agents (chlorine and bromine). If only the inductive effect operated in this case, vinylphosphonic dialkylamides would combine with compounds of the type X–H as readily as tertiary phosphine oxides.

Since vinyl compounds of four-coordinated phosphorus combine with nucleophilic agents and polymerise with greater difficulty than the corresponding carbonyl compounds, the conjugation of the heteroatom with the double bond is weaker in this case. Dipole moment measurements have shown that the conjugation of the phosphorus atom with a triple bond is more pronounced than with a double bond[298].

Of the general properties of compounds with unsaturated groups at the phosphorus atom, their inability to undergo disproportionation reactions, in contrast to the analogous antimony and bismuth compounds, should also be mentioned[299]:



Isomerisation processes of alkenylphosphonic esters in the presence of alkali metal alkoxides on heating merit attention. The phosphonates are then converted into species with maximum conjugation of the multiple bond [300-302]:

$$CH_2{=}CH{-}CH_2{-}P(OC_2H_5)_2 \xrightarrow{C_2H_5ONa} CH_3CH{=}CHP(OC_2H_5)_2,$$

$$CH_3CH{=}CHCH_2P(OR)_2 \xrightarrow{RONa} C_2H_5CH{=}CHP(OR)_2,$$

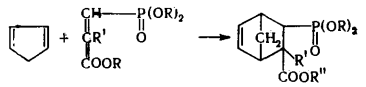
$$H_2C{=}C{=}CH{-}P(OR)_2 \xrightarrow{RONa} CH_3C{\equiv}C{-}P(OR)_2.$$

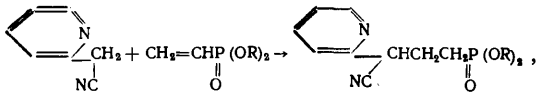
We shall now consider in detail various examples of nucleophilic addition to alkenylphosphonates. Reactions of this type have been investigated most fully for vinylphosphonic acid and have already been treated systematically to some extent [54]. The principal investigations in this field have been carried out by Pudovik, Kabachnik, and their coworkers. Since these reactions have the same mechanism, Pudovik called them "phosphonoethylation" [54], which reflects very correctly the essential features of this type of condensation addition. The reaction takes place readily with alcohol [303-305], hydrogen sulphide, mercaptans and selenium derivatives [17,297,306-311], ammonia and amines [312,313], various phosphorus(III) acids [314-317], thioacetic acid [318], and also thioacetic and malonic esters [309,310,315,319,320]. All the reactions with reagents of the type X – H have the same mechanism and take place as a rule in the presence of alkali metal alkoxides:

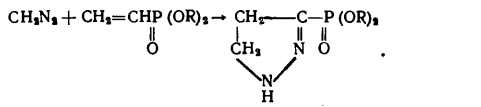
$$X{-}H + CH_2{=}CHP(OR)_2 \xrightarrow{RONa} XCH_2CH_2P(OR)_2,$$

where X = OR, SR, SeAr, NR_2, $P(O)(OR)_2$, $C(NO_2)_3$, etc.

Diene synthesis with vinylphosphonates and also reactions with the nitrile and esters of 2-pyridylacetic acid [321] and diazomethane [322] belong to the same class:







Dienylphosphonates also enter into nucleophilic addition reactions, with preferential 1,4-addition [127,308,323]:

$$CH_2{=}CH{-}C{=}CH{-}P(OR)_2 + X{-}H \xrightarrow{RONa} XCH_2CH{=}CCH_2P(OR)_2,$$

where X = SR, NR_2, or $P(S)(OR)_2$. Diene synthesis with these substances is possible but, in contrast to vinylphosphonates, here they constitute the diene component [324].

Recently the nucleophilic addition reactions have been extended to derivatives of acetoxyvinylphosphonic acid [325], triphenylvinylphosphonium bromide [326,327], alkynylphosphonates [328], vinylphosphonites [11], and perfluoroalkenylphosphonates [78,79,283,329,330].

b. Addition of reagents of the type —Hal. Addition to alkenylphosphonates of compounds with an active X–Hal bond has only just begun to be studied, if one disregards certain earlier investigations of the chlorination and bromination of these compounds [290]. In 1963 Schicke and Schrader took out a patent for the application of the products of the addition of alkanesulphenyl chlorides to vinylphosphonates [331]. At the same time and independently of these investigators similar studies were carried out by Ivin and coworkers [332]. It was found that the addition takes place in accordance with the polarisation of the sulphenyl chloride molecule, which corresponds to the formula RS^+Cl^-:

$$C_2H_5SCl + CH_2{=}CHP(OR)_2 \rightarrow ClCH_2CH(SC_2H_5){-}P(OR)_2,$$

$$C_2H_5SCl + CH_2{=}CHCH_2P(OR)_2 \rightarrow C_2H_5SCH_2CHClCH_2P(OR)_2.$$

The reaction was extended to a wide range of alkenylphosphonates and sulphenyl chlorides. Further development of the reaction showed that sulphur derivatives such as arenesulphenyl chlorides, alkyl dithiochlorides [333] [Ref. 333 refers to reaction of 2-chloroethyldithiochloride with derivatives of vinyl(alkyl)phosphic acid (Ed. of Translation)], sulphur dichloride [334], and acetyl dithiochloride [335] [Ref. 335 refers to acylsulphenyl chlorides (Ed. of Translation)] can enter into it:

$$CH_2{=}CHP(OR)_2 + \begin{cases} ClSCl \rightarrow ClCH_2CH(SCl){-}P(OR)_2 \\ ArSCl \rightarrow ClCH_2CH(SAr){-}P(OR)_2 \\ 2\,CH_3COCl \xrightarrow{-CH_3COCl} ClCH_2CH(SSCOR){-}P(OR)_2 \end{cases}.$$

Similar reactions have been carried out with allylphosphonates. Later it was shown that vinyl- and allyl-phosphonates react with nitryl chloride and hypochlorites [336,337]:

$$CH_2{=}CH(CH_2)_nP(OR)_2 + NO_2Cl \rightarrow O_2NCH_2CH(Cl)(CH_2)_nP(OP)_2,$$

$$CH_2{=}CH(CH_2)_nP(OR)_2 + (CH_3)_3C{-}O{-}Cl \rightarrow (CH_3)_3C{-}O{-}CH_2CH(Cl)(CH_2)_nP(OR)_2,$$

where n = 0 or 1.

The structure of the addition products was proved by their dehydrochlorination and by the ozonolysis of the unsaturated compounds produced.

Addition reactions in the presence of initiators of radical processes are possible with certain alkynylphosphines [19,20]:

$$C_2H_5SH + h\nu \rightarrow C_2H_5S^{\cdot} + H^{\cdot},$$

$$R_2PC{\equiv}CH + C_2H_5S^{\cdot} \rightarrow R_2PC^{\cdot}{=}CHSC_2H_5,$$

$$R_2PC^{\cdot}{=}CHSC_2H_5 + C_2H_5SH \rightarrow R_2PCH{=}CHSC_2H_5 + C_2H_5S^{\cdot}.$$

c. Oxidation and reduction reactions. It has been shown that in the presence of the usual hydrogenation catalysts such as platinum, palladium, and Raney nickel, hydrogen readily adds to double bonds without involving the P=O group [338-340]:

$$\begin{matrix} p\text{-}ClC_6H_4 \\ CH_3OC_6H_4 \end{matrix}\!\!> C{=}CH{-}P(OH)_2 \xrightarrow{H_2;\,Pd} \begin{matrix} p\text{-}ClC_6H_4 \\ CH_3OC_6H_4 \end{matrix}\!\!> CHCH_2P(OH)_2.$$

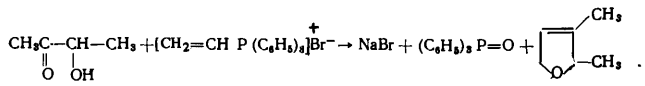
Rosental and Geyer made a successful attempt to oxidise allylphosphonates by the Bayer–Williger method [341]:

$$CH_2{=}CHCH_2P(OR)_2 + HCOOH + H_2O_2 \rightarrow CH_2{-}CH(OH){-}CH_2{-}P(OR)_2.$$

Pudovik and Gareev found that, in contrast to vinylphosphonates, allylphosphonates react with diazoacetic ester [342]:

$$CH_2{=}CHCH_2P(OR)_2 + N_2CH{-}COOC_2H_5 \rightarrow CH_2{-}CH(CHCOOC_2H_5){-}CH_2{-}P(OR)_2 + N_2.$$

Finally, we may note the capacity of triphenylphosphonium bromide to form cyclic compounds with α-hydroxycarbonyl compounds with simultaneous elimination of triphenylphosphine oxide[343,344]:



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Copolymerisation of Cyclic Compounds

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The number of studies dealing with the synthesis of copolymers and the investigation of the copolymerisation of cyclic monomers of a single class is large. The present review is concerned with the polymerisation of cyclic compounds, in which the ring is opened, with monomers of other classes, i.e. of a different chemical type. These processes include the copolymerisation of a number of cyclic compounds with olefins and also the copolymerisation of two cyclic compounds of different classes. The conditions of synthesis, the mechanism of formation, and certain properties of such copolymers are considered. The bibliography comprises 88 references.

CONTENTS

I. Introduction 681
II. Copolymerisation of cyclic compounds with olefins 682
1. Ionic copolymerisation 682
2. Radical copolymerisation 684
III. Copolymerisation of cyclic compounds 686
1. Copolymerisation of lactones 686
2. Copolymerisation of aziridines 689
3. Copolymerisation of anhydrides 690
4. Other types of copolymerisation 691

I. INTRODUCTION

The study of copolymerisation is of great practical and theoretical importance. Copolymerisation permits the desired modification of the properties of polymers. Sometimes the properties of copolymers differ appreciably from those of the corresponding homopolymers, while in other cases the copolymers combine the properties characteristic of the homopolymers.

The copolymerisation of vinyl monomers has been investigated comparatively thoroughly. Many reviews and monographs describing both the theoretical aspects of the process and the problems of the practical application of various copolymers have been published. The polymerisation and copolymerisation of cyclic compounds has been studied much less adequately. However, the number of papers published in this field increases from year to year.

The polymerisation of cyclic compounds has assumed increasing importance as a general method of synthesis of high-molecular compounds. The principal advances in this field were achieved in the industrial polymerisation of lactams, epoxy-compounds, and certain other cyclic monomers.

In the copolymerisation of cyclic compounds the following principal cases can be distinguished: (1) copolymerisation of cyclic compounds of the same chemical type (for example different lactones or epoxy-compounds); (2) copolymerisation of cyclic compounds with vinyl compounds; (3) copolymerisation of cyclic compounds of different chemical types (for example lactones with epoxy-compounds, etc.). From the theoretical standpoint, the first case is not of fundamental interest, since, in view of the identical chemical type of the monomers, the polymerisation mechanism does not differ from the mechanism of homopolymerisation and the process is determined merely by the kinetic and thermodynamic factors associated with the structure of the monomers. In contrast, the last two cases are extremely interesting from both the theoretical and practical points of view. They give rise to new opportunities for the synthesis of high-molecular compounds both as regards the development of new methods and the synthesis of new copolymers, and they extend the range of monomers suitable for copolymerisation.

The study of the copolymerisation of cyclic compounds has not been as detailed as that of vinyl monomers and the copolymerisation of cyclic compounds with compounds of other chemical types has been studied to an even lesser extent. There is no doubt, however, that such copolymerisation is of great interest and an attempt is made in the present review to give a systematic account of the available literature data on this question.

Polymerisation with ring opening is frequently called polyaddition. It takes place in stages (for example, hydrolytic polymerisation) or is a chain reaction (for example, ionic polymerisation). In the polymerisation of cyclic compounds the products are hetero-chain polymers, which can be obtained also by the polycondensation of certain bifunctional compounds. However, a characteristic feature of the polymerisation of cyclic compounds is that the compositions of the monomer and polymer are the same, i.e. in polymerisation with ring opening chemical bonds of types other than those in the monomer are not produced, the bonds being merely redistributed. Thus the initial monomer and the polymer formed in the polymerisation of cyclic compounds belong to the same chemical class.

Polymerisation has a number of advantages over polycondensation. Thus, in order to obtain polymers with high molecular weight by polycondensation, the proportions of the starting components must be rigorously equimolar and provision must be made for sufficiently effective removal from the reaction sphere of the low-molecular products evolved. In the polymerisation of cyclic compounds this is not necessary and the polymers formed have as a rule a high molecular weight.

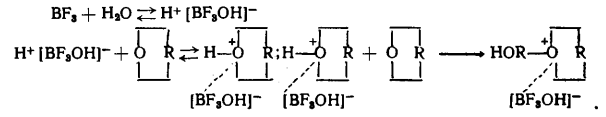
II. COPOLYMERISATION OF CYCLIC COMPOUNDS WITH OLEFINS

The copolymerisation of cyclic compounds with olefins has been investigated relatively little. It usually takes place via an ionic, usually cationic, mechanism, although there are indications that this type of polymerisation occurs also in the presence of radical initiators. Examples of this kind of polymerisation are quoted in Table 1.

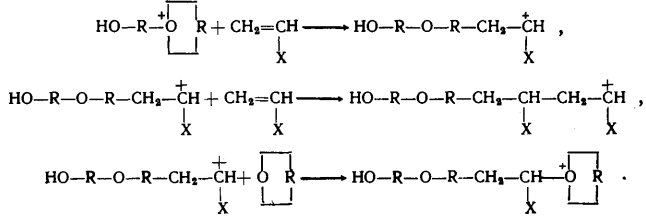
1. Ionic Copolymerisation

a. Cationic copolymerisation. The copolymerisation of cyclic compounds with olefins takes place mainly by a cationic mechanism, which may be because of the particular range of co-monomers investigated at the present time. These are mainly cyclic ethers, lactones, and certain other oxygen-containing compounds.

The initiation of the polymerisation of cyclic ethers in the presence of Lewis acids can be represented as follows:



When this mechanism is extended to the copolymerisation of cyclic ethers with olefins, the formation of copolymers can be represented thus:

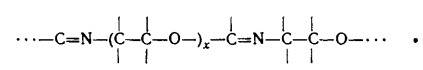


The possibility of the cationic copolymerisation of cyclic ethers and olefins was demonstrated by Merten[1], who achieved the copolymerisation of the following combinations of monomers in the presence of boron trifluoride-ether: styrene–olefin (propene, styrene) oxide, styrene–epichlorohydrin, chloroprene–olefin (propene, styrene) oxide, propene oxide–olefin (isobutene, propene, divinylbenzene), and epichlorohydrin–acrylonitrile. The copolymerisation yielded liquid copolymers. Liquid polyesters with terminal hydroxy-groups are formed in the cationic copolymerisation of epichlorohydrin with styrene in the presence of linear polyacetals and boron trifluoride-ether[2]. In contrast to the previous investigations, Minoura and Minton[3] obtained solid copolymers of epichlorohydrin and styrene by carrying out the reaction in benzene solution in the presence of boron trifluoride-ether. In the first stages of the reaction the copolymer is enriched in epichlorohydrin units. The authors suggest that the first reaction step is the interaction of epichlorohydrin with the catalyst. Gurgiolo[4] described a method for the preparation of solid copolymers

of epoxyalkanes with a number of unsaturated monomers, the copolymers having relatively high softening points (120–190°C) and readily forming very flexible films. The copolymerisation of epoxy-compounds (epichlorohydrin, epoxyethane, epoxypropane) with unsaturated compounds (vinylidene chloride, methyl methacrylate, butadiene) was carried out in the presence of the complex of ferric chloride and the epoxy-compound.

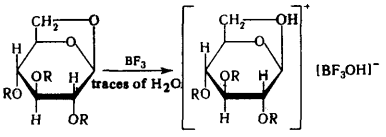
Durgaryan and Beginyan[5] described the copolymerisation of epichlorohydrin with aceto- and benzo-nitriles carried out in the solid phase at 70°C in the presence of 5 mole % $SnCl_4$ as catalyst. It is interesting that, under the conditions chosen, the nitriles taken separately do not polymerise. The formation of copolymers was demonstrated by fractional precipitation. In addition it was shown that the dependence of the composition of the copolymers on that of the initial mixture follows the equation characterising the composition of a copolymer. The copolymerisation constants are $r_1 = 4.2 \pm 0.4$ and $r_2 = 0 \pm 0.02$ for epichlorohydrin and acetonitrile and $r_1 = 2.8 \pm 0.2$ and $r_2 = 0 \pm 0.02$ for epichlorohydrin and benzonitrile.

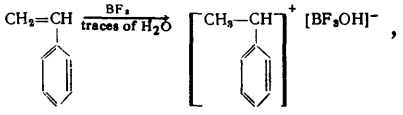
Since in the hydrolysis of copolymers the acids corresponding to the nitrile are formed quantitatively, together with compounds containing amino-groups, it was concluded that the copolymerisation of nitriles with epichlorohydrin does not involve the formation of new carbon–carbon bonds. The following structure was assigned to the copolymer:



Parnikis et al.[6] investigated the copolymerisation of trimethyl-laevoglucosan with styrene under the influence of boron trifluoride-ether. The formation of a copolymer was demonstrated by fractional precipitation, turbidimetric titration, and by thermomechanical compression curves. The following mechanism is proposed for the formation of copolymers.

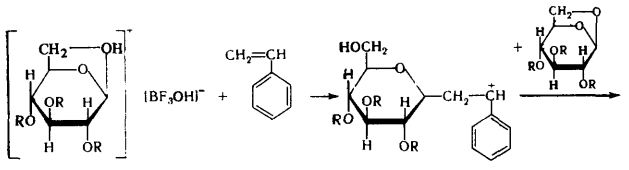
(a) Initiation:

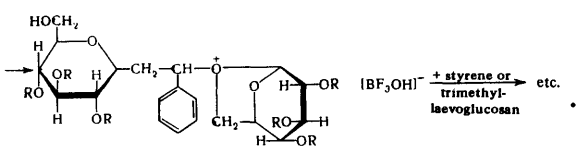




or

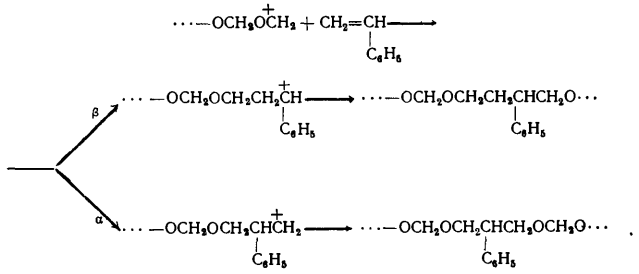
(b) chain growth:



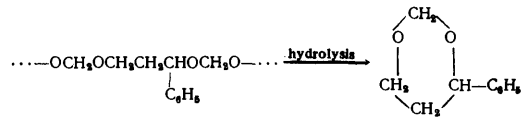


Parnikis et al.[6] believe that, in view of the different reactivities of the oxonium and carbonium ions, initially styrene polymerises preferentially and then trimethyl-laevoglucosan. When styrene or methylmethacrylate is allowed to act on the "live" tetramethyl-laevoglucosan polymer obtained under the influence of boron trifluoride, the corresponding block-copolymers are produced.

Trioxan (a cyclic ether) can also enter into cationic copolymerisation with styrene, vinyl ethers, and acrylonitrile[7]. It is suggested that the copolymerisation of trioxan with styrene takes place under the action of free carbonium cations. The polymeric chain can grow by the addition of a carbonium ion derived from trioxan to the α- or β-carbon atom of the vinyl group in styrene[8]:



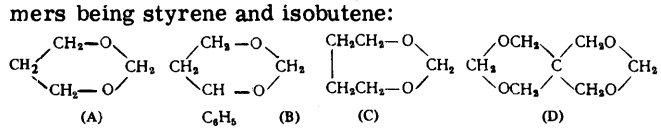
4-Phenyl-1,3-dioxan was isolated after the acid hydrolysis of the copolymer[9]:



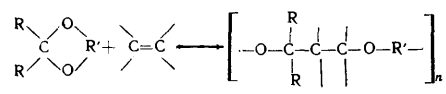
This is evidence of the addition of the carbonium ion to the β-carbon atom of styrene.

There are indications in the literature that the copolymers obtained in the cationic copolymerisation of trioxan with vinyl monomers are thermostable products capable of being worked by pressing (at 190°C and a pressure of 105 atm)[10]. Such copolymers can be used for the manufacture of flexible strips and films[11]. In order to copolymerise dioxan with vinyl monomers, catalysts other than boron triofluoride–ether can be used, for example triethyl or trimethyl hexachloroantimonate, bis(triethyloxonium) hexachlorostannate, trimethyl-, triethyl-, or tri-n-propyloxonium fluoroborate, etc.[11]

Cyclic formals have been polymerised with vinyl compounds[12]. The copolymers thus obtained are low-molecular liquid products with terminal hydroxyls. They are recommended for use in the synthesis of polyurethane rubbers. The cyclic formals used were 1,3-dioxan (A), 4-phenyl-1,3-dioxan (B), tetramethyleneformal (C), and the diformal derived from pentaerythritol (D), the vinyl monomers being styrene and isobutene:

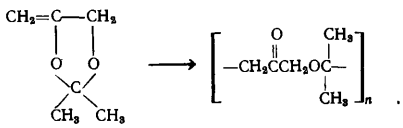


Sulphuric acid or polystyrenesulphonic acid and glycols such as butane-1,4-diol or 1,4-di-(β-hydroxyethoxy)butane were used as catalytic systems. It is suggested that copolymerisation leads to the formation of a copolymer having the following structure:



Okada and coworkers[13] investigated the cationic copolymerisation of 1,3-dioxolan with styrene in toluene solution at 25°C in the presence of boron trifluoride-ether. On the basis of the results obtained after the extraction of the product with hot water and methanol, it is suggested that a true copolymer is formed. The apparent constants for the copolymerisation of 1,3-dioxolan with styrene calculated from the Mayo–Lewis equation are respectively $r_1 = 1.9$ and $r_2 = 0.35$. It has been shown by NMR and by hydrolysing the copolymer that the 1,3-dioxolan ring opens during the reaction at the O_1-C_2 bond.

An interesting example of the formation of polymers involving the opening of the ring and of the multiple bond is the homopolymerisation of 2,2-dimethyl-4-methylene-1,3-dioxolan. Goodman and Abe[14] showed that, in the presence of boron trifluoride-ether, the polymerisation of 2,2-dimethyl-4-methylene-1,3-dioxolan takes place both with participation of the vinyl group and via ring opening and is accompanied by intramolecular rearrangement:



Lactones constitute another type of cyclic compounds capable of undergoing cationic copolymerisation with olefins. The copolymerisation takes place in the presence of stannic chloride or boron trifluoride-ether[15,16]. It has been found that cross propagation takes place with difficulty and under the conditions investigated appreciable amounts of block copolymers are formed. The authors explained this result by the formation in the reaction sphere of a specific complex of the lactone and the catalyst ($SnCl_4$) which catalyses the polymerisation of the lactone but not that of styrene. The authors note that the polymerisation of styrene and its copolymerisation with the β-lactone depend on the content of free catalyst (for example $SnCl_4$) in the reaction mixture, which is determined by the polarity of the solvent in which the copolymerisation is carried out.

In a polar solvent (for example in nitrobenzene) the amount of free stannic chloride increases. The content of lactone units in the copolymer is then reduced.

Although the nature of the complex of the lactone and the catalyst is unknown, the results obtained and also comparison with its catalytic capacity in homopolymerisation (for example of phthalide) show that the formation of the catalyst–cyclic monomer complex is an important factor controlling the copolymerisation of vinyl and cyclic compounds.

b. Anionic Copolymerisation. The anionic copolymerisation of vinyl monomers with cyclic compounds is carried out in the presence of initiators which form either free or co-ordinately bound anions. Under these conditions copolymerisation is rare—usually the homopolymerisation of both the cyclic and the vinyl monomer takes place.

Table 1 lists the known examples of anionic copolymerisation of cyclic compounds, mainly epoxy-compounds, with olefins. Thus Tsuruta and Fujio[17] showed that, in the presence of catalysts such as aluminium alkoxides, methyl vinyl ketone copolymerises with certain epoxy-compounds (epoxypropane or epichlorohydrin). The copolymerisation was carried out in benzene solution at 80°C for three days. The formation of a real copolymer is indicated by the agreement between the results of its investigation by turbidimetric titration and by infrared spectroscopy. Since the infrared spectrum of the copolymer does not contain absorption bands characteristic of the double bond and there are bands corresponding to the carbonyl group, it is suggested that the copolymerisation involves the opening of the ring of the epoxy-compound and of the double bond of the olefin.

Okamura and Hayashi[18] described the copolymerisation of olefins (ethylene, propene) oxides with acrylonitrile under the influence of γ-radiation. Successful copolymerisation depends to a considerable degree on the reaction temperature: at room temperature only the homopolymer of acrylonitrile is formed, while at low temperatures (between −178 and −196°C) copolymers are produced. As the reaction temperature is reduced, the content of olefin oxide units in the copolymer increases. The fact that epoxypropane does not polymerise by a radical mechanism and also the occurrence of the reaction at low temperatures suggest an anionic reaction mechanism in this case, but special studies designed to elucidate the mechanism of copolymerisation were not undertaken.

Lactones are also capable of polymerising with certain unsaturated compounds under the influence of anionic catalysts. Shimosaka et al.[19] carried out the copolymerisation of β-propiolactone with acrylonitrile at room temperature in the presence of various anionic catalysts: $SrZn(C_2H_5)_4$, $Al(C_2H_5)_3$, naphthalenesodium, $C_4H_9Li + Al(C_2H_5)_3$, and $B(C_4H_9)_3 + Cd(C_2H_5)_2$. Copolymerisation results in the formation of polymeric products which can be separated into fractions soluble and insoluble in chloroform. The chloroform-soluble fraction is the homopolymer of β-propiolactone, while the insoluble fraction consists of the homopolymer of acrylonitrile and its copolymer with β-propiolactone.

Shiota et al.[20] achieved the grafting of β-propiolactone onto polyacrylonitrile. Potassium hydroxide, sodium methoxide, and butyl-lithium were used as catalysts of the graft copolymerisation of the β-lactone with polyacrylonitrile.

Apart from the copolymerisation reactions of cyclic compounds with olefins examined above, examples of block-copolymerisation are known. Thus Richards and Szwarc[21] and also Finaz et al.[22] obtained block-copolymers of styrene with epoxyethane. The reaction of "live" polystyrene with epoxyethane results in the formation of terminal ... $CH_2CH_2\bar{O}\dot{N}a$ group, capable of adding epoxyethane with formation of copolymers in which the polystyrene block is included between polyepoxyethane blocks. Such copolymerisation goes almost to completion. When the same reaction is carried out with epoxypropane, only 25% of the epoxy-compound copolymerises. Probably in this case chain transfer to epoxypropane takes place and leads to the formation of a polyepoxypropane homopolymer. Furukawa et al.[23] obtained a block-copolymer of acrylonitrile with epoxyethane, using the alkoxide of polyepoxyethane as the catalyst.

2. Radical Copolymerisation

The radical copolymerisation of olefins with cyclic compounds has been least investigated. Indeed, while the addition of free radicals to atoms attached to a double bond has been known for a long time[24], the process has been inadequately elucidated for various cyclic compounds. In general radicals show a greater tendency to combine with hydrogen or any other reactive atom or group than to effect ring opening. Probably this is why radical copolymerisation of olefins with cyclic compounds is difficult.

Nevertheless cases are known where carbon and other rings open under the influence of free radicals. This has been demonstrated in reactions of low-molecular organic

compounds. For example, in the free-radical chlorination of spiropentanes chloro-derivatives of aliphatic hydrocarbons are formed[25].

Gritter[26] achieved the addition of epoxypropane to oct-1-ene in the presence of t-butyl peroxide; 2-undecanone (a) and 5-hydroxy-2-hexanone (b) were isolated in low yields. By carrying out the reaction at a lower temperature (below 125°C), it proved possible to obtain only the second compound. The authors suggest the following reaction mechanism:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\,(CH_3)_3CO\cdot ,$$

$$(CH_3)_3CO\cdot + CH_3CH(O)CH_2 \longrightarrow CH_3\dot{C}(O)CH_2 \longrightarrow CH_3C(=O)\dot{C}H_2 ,$$

$$CH_3C(=O)\dot{C}H_2 + CH_2{=}CHC_6H_{13} \longrightarrow CH_3C(=O)CH_2CH_2\dot{C}HC_6H_{13} \xrightarrow{RH} CH_3C(=O)CH_2CH_2CH_2C_6H_{13}, \quad (a)$$

$$CH_3C(=O)\dot{C}H_2 + CH_3CH(O)CH_2 \longrightarrow CH_3C(=O)CH_2CH_2CH(OH)CH_3 . \quad (b)$$

Radicals formed from epoxypropane isomerise to keto-radicals, which are capable of reacting both with the double bond and with the epoxy-ring. Further development of the reaction is difficult due to termination which occurs when the radicals react with hydrogen atoms. The last of the stages enumerated above prevents the formation of a polymeric chain. However, despite the absence of communications on the homopolymerisation of olefin oxides under the action of radical initiators, the possibility of ring opening by a radical mechanism cannot be excluded[25,27]. Nor can one exclude the possibility of the copolymerisation of olefins with cyclic compounds, the occurrence of which has been confirmed in a number of studies quoted below. Examples of the radical copolymerisation of certain cyclic compounds, mainly epoxy-compounds, with olefins are presented in Table 1.

Table 1. Copolymers of cyclic compounds and olefins.

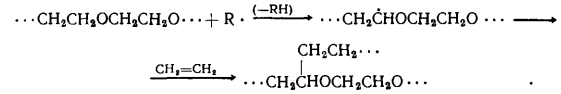
Co-monomers	Type of catalyst: radical	anionic	cationic	Refs.
Epoxyethane-				
-ethylene	benzalazine	–	–	28
-vinylidene chloride	potassium persulphate	–	$FeCl_3$.epoxypropane	30, 4
-chlorotrifluoroethylene	t-butyl peroxide	–	–	34
-perfluoropropene	ditto	–	–	34
-butadiene	–	–	$FeCl_3$.epoxypropane	4
-styrene	–	–	naphthalenesodium	21
	–	–	phenylisopropyl-potassium or methylstyrene tetramer	22
Epoxypropane-				
-vinylidene chloride	potassium persulphate	–	$FeCl_3$.epoxypropane	30, 4
-propene	–	–	BF_3-ether	1
-isobutene	–	–	ditto	1
-butadiene	–	–	$FeCl_3$.epoxypropane	4
-chloroprene	–	–	BF_3-ether	1
-methyl methacrylate	–	–	$FeCl_3$.epoxypropane	4
-methyl vinyl ketone	–	tri-isopropyl-aluminium	–	17
-styrene	–	naphthalene-sodium	BF_3-ether	1, 2, 23
-divinylbenzene	–	–	ditto	1
Epichlorohydrin-				
-vinylidene chloride	–	–	$FeCl_3$.epoxypropane	4
-butadiene	–	diethylzinc + nickel or cadmium di-halide-di(tri-alkyl)phosphite	ditto	4, 38
-methyl methacrylate	–	–	"	4
-styrene	–	–	BF_3-ether	1, 2, 3
-acrylonitrile	–	–	ditto	1
-acetonitrile	–	–	stannic chloride	5
-benzonitrile	–	–	ditto	5
-methyl vinyl ketone	–	tri-isopropyl-aluminium	–	17
Chloroprene oxide-				
-vinylidene chloride	–	–	$FeCl_3$.epoxypropane	4
-butadiene	–	–	ditto	4
-methyl methacrylate	–	–	"	4
Butadiene oxide-				
-vinylidene chloride	potassium persulphate	–	–	30
Styrene oxide-				
-butadiene	cumenyl hydro-peroxide sodium sulphate	–	–	31
-chloroprene	–	–	BF_3-ether	1
-styrene	–	–	ditto	1

Table 1. (cont'd).

Co-monomers	Type of catalyst: radical	anionic	cationic	Refs.
Trioxan-				
-acrylonitrile	–	–	*p*-nitrophenyl-diazonium fluoroborate	11
-styrene	–	–	BF_3-ether	7, 8
-vinyl acetate	–	–	ditto	7
-isobutyl vinyl ether	–	–	"	10
-methyl vinyl ketone	–	–	"	7
1,3-Dioxolan-				
-isobutene	–	–	sulphuric acid or polystyrenesulphonic acid	12
-styrene	–	–	BF_3-ether	12, 13, 39
4-Phenyl-1,3-Dioxolan-				
-isobutene	–	–	sulphuric acid or polystyrenesulphonic acid	12
-styrene	–	–	ditto	12
4-Chloromethyl-1,3--dioxolan				
-styrene	–	–	BF_3-ether	39
Tetramethyleneformal-				
-isobutene	–	–	sulphuric acid or polystyrenesulphonic acid	12
-styrene	–	–	ditto	12
Diformal of pentaerythritol-				
-isobutene	–	–	"	12
-styrene	–	–	"	12
Trimethyl-laevoglucosan-				
-styrene	–	–	"	6
β-Propiolactone-				
-ethylene	di-t-butyl peroxide	–	–	32
-styrene	–	–	stannic chloride, BF_3-ether	15, 16
-acrylonitrile	–	naphthalene-sodium, tri-ethylaluminium, butyl-lithium-tri-ethylaluminium, tributyl-boron-diethyl-cadmium	–	19, 40
-polyacrylonitrile	–	butyl-lithium, potassium hydroxide, sodium methoxide	–	20

The radical copolymerisation of 1,2-epoxy-compounds with olefins takes place mainly at high temperatures. Coffman[28] described the copolymerisation of ethylene with epoxyethane, which was carried out at 200–250°C under a pressure of 350–1000 atm in the presence of benzalazine as the initiator. The copolymers obtained contained between 5 and 15 mole % of epoxyethane. When the copolymer was treated with hydrobromic acid, most of the epoxyethane units were eliminated in the form of ethyl bromide. This shows that most of these units are arranged consecutively in the copolymer and that the latter is an antistatic agent. Furthermore polyepoxyethane, which can form by a non-radical mechanism, as a result of the presence of ether

links in the main chain, can readily give up hydrogen atoms to radicals. Consequently there is a possibility of the formation of graft copolymers via a chain-transfer reaction:



In 1949 a method for the copolymerisation of dec-1-ene with epoxyethane was patented[29]. The reaction was carried out at 260–370°C for 10 h.

Stanton and Lowry[30] obtained a series of copolymers of vinylidene chloride with the oxides of ethylene, propene, and butadiene. The copolymerisation was carried out in aqueous emulsion using potassium persulphate as the initiator. In contrast to the unmodified poly(vinylidene chloride), the copolymers with epoxyethane had lower softening temperatures (about 135°C) and contained polyepoxyethane, which could not be extracted with water. However, this is not sufficient evidence for postulating the formation of a non-ordered copolymer.

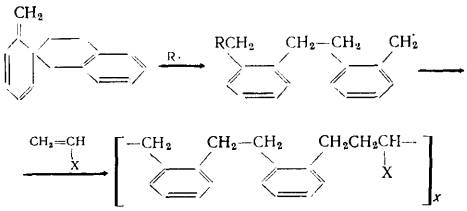
Ponomarev et al.[31] described a study on the copolymerisation of styrene oxide with butadiene in the presence of cumenyl hydroperoxide. It was shown that the polymerisation of styrene oxide and butadiene in aqueous emulsion at 5°C leads to the formation of a copolymer with a high molecular weight.

McCall and Coover[32] described a method for the preparation of copolymers of ethylene and β-propiolactone containing 2.8 wt. % of the lactone. The copolymerisation was performed in the presence of di-t-butyl peroxide.

The copolymerisation of styrene with β-propiolactone in the presence of radical initiators led to the formation of block-copolymers with terminal hydroxy- and carbonyl groups[33].

It is noteworthy that in all the studies enumerated above there are no direct data demonstrating that the addition of cyclic compounds to the growing polymeric molecule takes place via ring opening by a radical mechanism. In general the radical copolymerisation of vinyl monomers with cyclic compounds takes place with difficulty. However, in special cases the process does occur and leads to the formation of copolymers with alternating units of the initial monomer. For example, Hauptschein and Lesser[34] achieved the radical copolymerisation of perfluoropropene with epoxyethane (both with initiation by ultraviolet light and in the presence of di-t-butyl peroxide), the monomer ratio in the initial mixture being varied from 1 : 1 to 2 : 1. In all cases polymeric products were obtained in the form of a thick viscous mass with high stability to the action of chemical reagents. The stability of this copolymer to the action of concentrated sulphuric acid and heating with 47% hydriodic acid for 24 h at 150°C suggests that the reaction product is a copolymer with alternating units of the initial monomers in proportions of 1 : 1, since otherwise it would have decomposed. Probably the chain of this copolymer is constructed on the "head to tail" principle, i.e. $-(C_3F_6-O-CH_2-CH_2-)$. Copolymers of epoxyethane with trifluoroethylene were obtained similarly. Vinylidene fluoride does not form copolymers with epoxyethane but the rate of homopolymerisation of vinylidene fluoride in the presence of epoxyethane is much higher.

Spirodi-*o*-xylylene may be quoted as a specific cyclic monomer, which in the presence of radical initiators is capable of homopolymerisation and copolymerisation with a number of olefins (styrene, acrylates, and methacrylates); its copolymerisation with many olefins yields copolymers with a 1 : 1 ratio of structural units[35]:



A distinct feature of this monomer is the presence of a double bond conjugated with the ring. This double bond evidently makes the monomer sensitive to radical initiators. In this case polymerisation takes place with the opening of the double bond and the conjugated ring, as in the polymerisation of conjugated dienes by 1,4-addition. 1,1-Dichloro-2-vinylcyclopropane[36] and vinylcyclopropane[37] polymerise in the same way, under the action of both cationic and radical catalysts.

III. COPOLYMERISATION OF CYCLIC COMPOUNDS

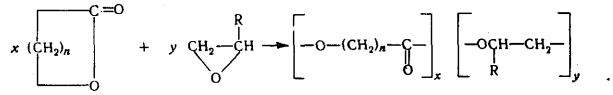
The copolymerisation of cyclic monomers can be used for the preparation of various classes of linear hetero-chain copolymers, which can find a wide variety of applications. Most of the studies which have been made dealt with the copolymerisation of cyclic compounds of the same chemical type, differing from one another only in the number of units in the ring or the presence of various substituents. A number of investigations have been made of the copolymerisation of lactams[41–45] and lactones[46,47]. The copolymerisation of various cyclic ethers has been discussed in detail in the monograph of Furukawa and Saegusa[48].

The present review deals with studies on the polymerisation of cyclic compounds of different chemical types. Copolymers with hetero-bonds in the macromolecular chain derived from both copolymerising monomers can be obtained in such copolymerisation. However, the number of studies on this type of copolymerisation is small and covers a very restricted range of monomers (Table 2).

1. Copolymerisation of Lactones

a. Copolymerisation with oxygen-containing compounds. Lactones can polymerise with cyclic ethers (epoxyalkanes, tetrahydrofuran, oxetans, trioxan), imines, and certain other cyclic compounds. The activity of lactones in the copolymerisation reaction is different and depends on the structure of the lactone, the chemical type and structure of the second co-monomer, and the catalytic system used.

The copolymerisation of lactones with epoxy-compounds should lead to the formation of copolymers containing ether and ester links in the chain:



This process has attracted the attention of many investigators, but satisfactory results cannot be always achieved. Thus Furukawa and coworkers[78] established that, when cadmium, zinc, or aluminium alkyls are used as catalysts

and oxygen, water, or alcohol as co-catalysts (i.e. catalytic systems which are fairly effective for the homopolymerisation of β-propiolactone[78] and epoxypropane[79]) in the copolymerisation of β-propiolactone with epoxypropane, a copolymer does not form. Catalytic systems such as boron trifluoride-ether and triethylaluminium with added water also proved to be ineffective[49]. A copolymer of β-propiolactone and epoxypropane could be obtained only in the presence of aluminium tri-isopropoxide but with a very low (up to 5%) content of epoxypropane units[49]. Cherdron and Ohse[50] also failed when they used organoaluminium compounds and boron trifluoride-ether as catalysts for this copolymerisation. Thus it is evident that the copolymerisation of β-propiolactone with epoxypropane in the presence of the above catalysts either does not take place at all or takes place with great difficulty.

In contrast to epoxypropane, other epoxy-compounds (epichlorohydrin, styrene oxide) undergo copolymerisation with β-propiolactone much more readily. The copolymerisation of β-propiolactone with epichlorohydrin[49,50] and styrene oxide[50] takes place readily in the presence of triethylaluminium, but boron trifluoride-ether and aluminium tri-isopropoxide proved to be ineffective as catalysts of the copolymerisation of epichlorohydrin with β-propiolactone[49].

In contrast to β-propiolactone, δ-valerolactone copolymerises comparatively readily with epoxypropane and styrene oxide in the presence of triethylaluminium or boron trifluoride-ether.

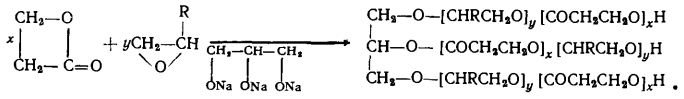
As a rule, the copolymers of lactones with epoxy-compounds are solid crystalline products with a molecular weight of several tens of thousands and with a melting point lower than those of the corresponding lactone-homopolymers. However, the use of polyhydric alcohols or the corresponding alkoxides as polyfunctional co-catalysts in the copolymerisation of lactones with epoxy-compounds leads to the formation of branched-chain liquid copolymers

Table 2. Copolymerisation of cyclic compounds.

Co-monomers	Type of catalyst: anionic	Type of catalyst: cationic	Refs.
β-Propiolactone–			
–epoxypropane	aluminium tri-iso-propoxide	–	49
–epichlorohydrin	triethylaluminium	BF_3-ether	49, 50
–styrene oxide	ditto	ditto	50
–butadiene monoxide	"	"	50
–isoprene monoxide	"	"	50
–allylglycidic ether	"	"	50
–vinylcyclohexene monoxide	"	"	50
–trioxan	–	"	50
–3,3-bis(chloromethyl)oxacyclobutane	triethylaluminium–water	"	52–54
–tetrahydrofuran	ditto	"	49
–aziridine	triethylamine	BF_3-ether, stannic chloride	55,56
–*N*-carboxy-anhydride of DL-valine	pyridine, sodium methoxide	–	57, 58
–phenyl ester of ethylene phosphorous acid	tertiary amines, alkali metal alkoxides	–	59
ββ-Dimethyl-β-propiolactone			
–3,3-bis(chloromethyl)oxacyclobutane	–	BF_3-ether	54
β-Methyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	ditto	54
α-Methyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	"	54
αα-Dimethyl-β-propiolactone–			
–3,3-bis(chloromethyl)-oxacyclobutane	–	"	54
γ-Butyrolactone–			
–trioxan	–	"	60
–aziridine	triethylamine	BF_3-ether, stannic chloride	55
δ-Valerolactone–			
–epoxypropane	triethylaluminium	BF_3-ether	50
–styrene oxide	ditto	ditto	50
ε-Caprolactone–			
–aziridine	triethylamine	BF_3-ether, stannic chloride	55
–ε-caprolactam	tri-isobutylaluminium, sodium	–	61
Aziridine–			
–ethylene carbonate*	–	–	62
–succinimide*	–	–	63
–glutarimide	–	BF_3-ether	63
–phthalimide	–	ditto	63
–epoxypropane	–	"	64–66
2-Methylaziridine–			
–succinimide	–	"	63
N-Butylaziridine–			
–phthalic anhydride*	–	–	67
N-Cyclohexylaziridine–			
–phthalic anhydride*	–	–	67
Succinic anhydride–			
–3-phenyl-2-oxazolidinone	lithium chloride, benzonitrile, tetraethylammonium chloride	*p*-toluenesulphonic acid, succinic acid, titanium tetrachloride	68
–5-phenoxymethyl-3-phenyl-2-oxazolidinone	ditto	ditto	68
–3,5-diphenyl-2-oxazolidinone	"	"	68
Phthalic anhydride–			
–epoxyethane	benzyldimethylamine	–	69
–epoxypropane	butyl-lithium, ethylmagnesium bromide, diethylmagnesium, diethylzinc, diethylcadmium	–	70
–epichlorohydrin	benzyldimethylamine	–	69
–epoxycyclohexane	ditto	–	69
–allylglycidic ether	"	–	69
–3-phenyl-2-oxazolidinone	lithium chloride, benzonitrile, tetraethylammonium chloride	*p*-toluene sulphonic acid, succinic acid, titanium tetrachloride	68
–5-phenoxymethyl-3-phenyl-2-oxazolidinone	ditto	ditto	68
–3,5-diphenyl-2-oxazolidinone	"	"	68
Tetrachlorophthalic anhydride–			
–butylglycidic ether	–	zinc chloride	71
Mixture of maleic and phthalic anhydrides–			
–epoxypropane	tetramethyleneammonium bromide, lithium chloride	–	72
Pyromellitic anhydride–			
–epichlorohydrin	triethylaluminium, lithium chloride, benzyldimethylamine	–	73
–phenylglycidic ether	ditto	–	73
–3,3-bis(chloromethyl)-oxacyclobutane	"	–	73
3-Phenyl-Δ⁴-tetrahydrophthalic anhydride–			
–epoxypropane	diethylzinc–(+)borneol	–	74
Epoxypropane–			
–propylene sulphide	alkali metal hydroxides	–	75
–butylene sulphide	–	complexes of iron chlorides with epoxypropane	76
–*N*-carboxy-anhydride of DL-alanine	triethylaluminium, diethylzinc, diethylzinc–water (alcohol), triethylaluminium–water, aluminium tri-isopropoxide, sodium methoxide, and diethylamine	–	77

* Without catalyst.

with terminal hydroxyls[50], which gives rise to wide opportunities for the modification of such copolymers by allowing them to react with isocyanates and other compounds:



Cherdron and Ohse[50] also studied the copolymerisation of lactones with epoxy-compounds containing unsaturated bonds. These were butadiene monoxide [epoxybutene ? (Ed. of Translation)], isoprene monoxide, allylglycidyl ether, and vinylcyclohexene monoxide. It was established that unsaturated epoxy-compounds which polymerise with difficulty via ring opening are also difficult to copolymerise with a lactone. The first three epoxy-compounds belong to this class. Vinylcyclohexene monoxide, which itself readily polymerises, is also easy to copolymerise with lactones. It is noteworthy that the choice of catalyst influences to a high degree the composition and properties of the copolymers formed. In the presence of boron trifluoride-ether liquid copolymers of β-propiolactone and vinylcyclohexene monoxide enriched in the second component are produced. On the other hand, in the copolymerisation of the same compounds in the presence of triethylaluminium solid copolymers enriched in β-propiolactone residues are produced. The presence of double bonds in such copolymers gives rise to the possibility of their further modification. For example, when the unsaturated epoxy-compound is copolymerised with a lactone in the presence of triethylaluminium in styrene, which does not polymerise under the influence of triethylaluminium without a co-catalyst, it is possible to achieve two-stage copolymerisation[50]. The first stage involves the formation of the copolymer of the lactone with the unsaturated epoxy-compound, and, after the addition of a radical initiator to the reaction mixture, the copolymerisation of styrene with the copolymer takes place.

Toda et al.[52,53] investigated the copolymerisation of β-propiolactone with 3,3-bis(chloromethyl)oxacyclobutane in the presence of "triethylaluminium–water" and boron trifluoride-ether catalytic systems. In both cases copolymers insoluble in chloroform were obtained. The formation of a copolymer was confirmed by infrared spectroscopy. With increasing content of lactone in the initial mixture, the degree of conversion and the fraction insoluble in chloroform decrease. When the initial mixture contains 75 mole % of 3,3-bis(chloromethyl)oxacyclobutane, only the homopolymer of the latter is formed. The composition of the copolymer depends to a large extent on the type of catalyst used in the copolymerisation. The copolymers obtained in the presence of triethylaluminium and water contain more lactone units than those produced in the presence of boron trifluoride-ether.

Tsuda et al.[54] studied the effect of substituents on the reactivity of lactones in cationic copolymerisation with 3,3-bis(chloromethyl)-oxacyclobutane. The activity of the lactone investigated, found from the composition of the copolymers, decreases in the following sequence: ββ-dimethyl-β-propiolactone ≫ β-methyl-β-propiolactone > β-propiolactone > α-methyl-β-propiolactone > αβ-dimethyl-β-propiolactone. The authors[54] believe that in the polymerisation of β-lactones the C–O bond dissociates on the side of the carbonyl group except in ββ-dimethylpropiolactone where it dissociates on the side of the alkyl groups.

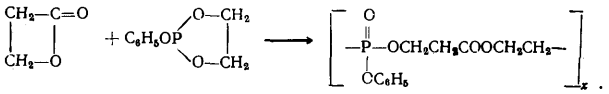
The copolymerisation of lactones with tetrahydrofuran[49] and trioxan[60] is also possible. Copolymers of tetrahydrofuran and β-propiolactone[50] have been obtained in the presence of the "triethylaluminium–water" catalytic system in the form of viscous liquids or resins. Trioxan has been copolymerised with γ-butyrolactam in the presence of boron trifluoride-ether[60].

Table 3 presents the copolymerisation constants of lactones and a series of cyclic ethers. The reactivity of the compounds undergoing copolymerisation, listed in Table 3, depends to some extent on the copolymerisation conditions: the nature of the catalyst, reaction temperature, etc.

Table 3. Constants for the copolymerisation of lactones with certain other cyclic compounds.

Copolymerising monomers		Copolymerisation constants		Catalyst	Refs.
1	2	r_1	r_2		
β-Propiolactone	styrene oxide	15.0	0.1±0.1	$Al(C_2H_5)_3$	50
ditto	epichlorohydrin	9.0	0.2±0.1	$Al(C_2H_5)_3$	50
"	tetrahydrofuran	0.4	2.9	$BF_3(C_2H_5)_2O$	49
"	ditto	0.1	5.5	$Al(C_2H_5)_3 - H_2O$	49
"	3,3-bis-(chloromethyl)oxacyclobutane	0.06	38	$BF_3(C_2H_5)_2O$ (at 0°)	52.53
"	ditto	0.04	30	$Al(C_2H_5)_3 - H_2O$ (at 0°)	52.53
"	"	0.05	16	$BF_3(C_2H_5)_2O$ (at −50°)	52.53
"	"	0.1	30	$Al(C_2H_5)_3 - H_2O$ (at −50°)	52.53
γ-Valerolactone	epichlorohydrin	5.3	0.25±0.1	$Al(C_2H_5)_3$	50

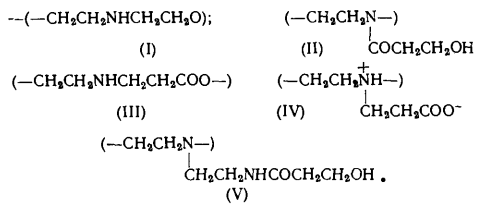
b. Copolymerisation of lactones with other cyclic compounds. Apart from the copolymerisation of lactones with cyclic ethers, cases are known where they were copolymerised with certain other cyclic compounds. The copolymerisation of lactones with cyclic phosphites is interesting[59]:



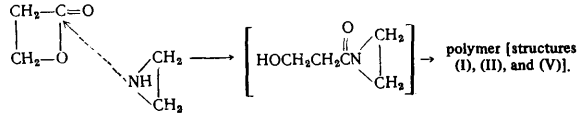
This results in the formation of a solid white polymer melting at 160°C. The reactions take place readily on heating (at or above 150°C) or even at room temperature in the presence of basic catalysts (tertiary amines, amides, alkali metal alkoxides, etc).

A few studies have been made on the copolymerisation of lactones with aziridines[55,56]. The copolymerisation of β-propiolactone, γ-butyrolactone, and ε-caprolactone with aziridine is catalysed by compounds such as boron trifluoride-ether, stannic chloride, triethylamine, sodium cyanide, and mercurous chloride[55]. Polymers with a low molecular weight were obtained in all cases. With increasing dielectric constants of the solvents in which the copolymerisation is carried out, there is an increase in the yield of copolymer. It is interesting to note that aziridine and β-propiolactone activate one another in the copolymerisation reaction and the latter can take place without catalysts[56]. The structure of the copolymer formed depends to a large extent on the dielectric constant of the solvent but is independent of the type of catalyst used[55,56]. On the basic of infrared spectroscopic data, the authors suggest that the formation of several different structures is possible

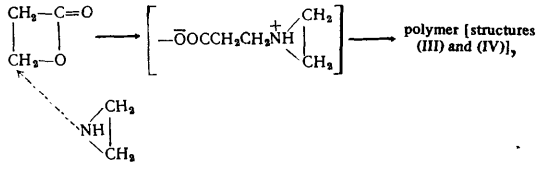
in the synthesis of the copolymer of β-propiolactone and aziridine:



The formation of a particular copolymer structure depends on the site of ring opening, which is in turn determined to a large extent by the polarity of the solvent used in the reaction. The role of the solvent as regards the variation of the site of ring opening is not entirely clear, but it may involve a change in the distribution of electron density of the monomer when the polar solvent adds to the carbonyl carbon of the lactone. In non-polar solvents the carbonyl carbon of the lactone is probably attacked by the nitrogen atom of aziridine:



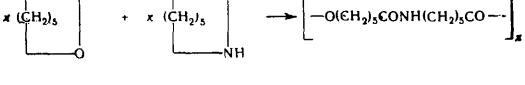
Here too copolymers with structure (I), (II), or (V) are formed. On the other hand, in polar solvents aziridine may attack the β-carbon atom of the lactone:



which results in the formation of copolymers with structures (III) and (IV).

Dermer and Ames[57,58] achieved the copolymerisation of β-propiolactone with the *N*-carboxy-anhydride of DL-valine in a mixture of anisole and benzene in the presence of pyridine and obtained a low-molecular copolymer (mol. wt. about 1150) in the form of a white powder with a softening temperature of 20°C. When the same reactants were copolymerised in the presence of sodium methoxide, it proved possible to increase somewhat both the molecular weight (about 3550) and the softening temperature of the copolymer (85°C).[57]

An interesting method for the preparation of polyamidoethers consists in the copolymerisation of ε-caprolactone with ε-caprolactam in the presence of tri-isobutylaluminium or sodium as catalysts[61]:

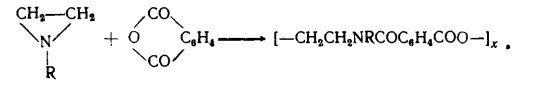


Thus lactones are capable of forming copolymers with a number of cyclic compounds; at the present time the copolymerisation of lactones with cyclic oxygen-containing compounds has been investigated in greatest detail.

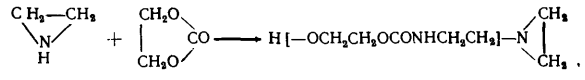
2. Copolymerisation of Aziridines

The copolymerisation of aziridine with lactones was described in the previous section[55,56]. Apart from this, examples of the copolymerisation of aziridines with certain other cyclic compounds are known.

N-Substituted polyamidoethers are formed in the copolymerisation of *N*-substituted aziridines (*N*-butylaziridine, *N*-cyclohexylaziridine) with dibasic acid anhydrides[67]:

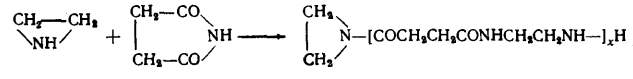


The copolymerisation of aziridines with cyclic carbonates leads to the formation of high-molecular polyurethanes with terminal hydroxy- and alkylimino-groups:



Copolymers with a degree of polymerisation up to 2000 have been obtained in the copolymerisation of aziridine with ethylene carbonate[62]. In both cases described above the copolymerisation was carried out by heating the initial monomers without any catalysts.

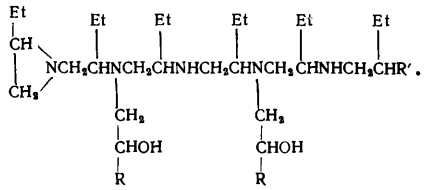
The copolymerisation of aziridines with cyclic imides, which leads to the formation of crystalline polyamides, is an interesting reaction[63]. Thus the copolymerisation of aziridine and succinimide yields a polyamide melting at about 300°C:



This reaction takes place particularly readily with compounds having small rings and constitutes an interesting method for the preparation of polyamides with short methylene chains. Crystalline polyamides have been obtained in the copolymerisation of the following monomer systems: 2-methylaziridine–succinimide, aziridine–glutarimide, and aziridine–phthalimide. The reactivity of imides in copolymerisation with ethyleneimine decreases in the following sequence: maleimide > phthalimide > succinimide > glutarimide > *N*-methylsuccinimide[63]. The copolymerisation of aziridines with imides can be carried out both with and without catalysts by heating the initial monomers. The presence of boron trifluoride-ether as catalyst for the copolymerisation of aziridines with cyclic imides favours the formation of a copolymer enriched in aziridine units, while the addition of triethylamine does not affect the composition of the copolymer[63].

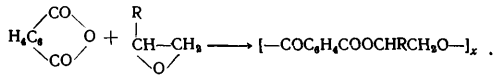
The copolymerisation of aziridines with epoxyalkanes has been described[64,80,81]. However, Overberger and Tobkes[65] have shown that the resulting copolymerisation products have a complex structure. In the copolymerisation of 2-ethylaziridine with 1,2-epoxy-compounds, they used Lewis acids as catalysts. In the presence of the most active catalyst, boron trifluoride-ether, copolymers with a polyimine structure are formed, in which the imino-groups are β-hydroxyalkylated by the 1,2-epoxy-compounds. Under the copolymerisation conditions investigated, the imine is more active than the epoxy-compound. Probably the polyimine chain grows to a considerable length before the epoxyalkane units are incorporated into it. The authors suggest that in the first stages of the copolymerisation, complexes of the catalysts with the imine residues of the

polymer are mainly formed, as a result of which the catalyst is incapable of inducing the polymerisation of the epoxy-compound. The authors attribute the following structure to the copolymer of 2-ethylaziridine and epoxydodecane:



3. Copolymerisation of Anhydrides

The copolymerisation of dicarboxylic acid anhydrides with epoxyalkanes leading to the formation of polyesters has been comparatively well investigated:

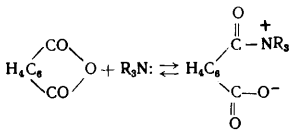


Fish and Hoffman[82-84] established that, in the copolymerisation of epoxy-compounds with anhydrides in the absence of catalysts, the epoxy-compounds are partially homopolymerised. In order to reduce the degree of homopolymerisation and to ensure more complete copolymerisation, the ratio of the anhydride to the epoxy-compound should be 0.85 : 1.[84,85]

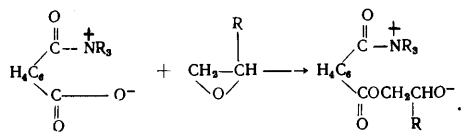
The use of catalysts favours the formation of polyesters. Fisher[69] showed that the polyesterification of dibasic acid anhydrides with epoxy-compounds in the presence of tertiary amines as catalysts takes place to the extent of 98–99% and the molecular weight of the polymers formed reaches about 18 500. The properties of the polyesters depend on the structure of the starting materials. The copolymerisation of epoxyethane with various anhydrides yields highly crystalline polymers which melt in the range 110–165 °C depending on the structure of the anhydride. The copolymerisation of epoxycyclohexane with anhydride yields polyesters melting above 100 °C. Structured polyesters are obtained in the copolymerisation of epoxy-compounds with maleic anhydride[71].

Fisher[69] proposed the following mechanism for the formation of polyesters in the copolymerisation of anhydrides with epoxy-compounds in the presence of amine catalysts.

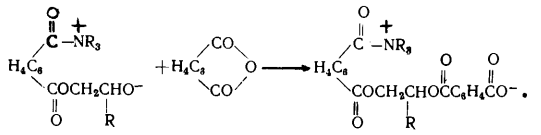
1. Activation of the anhydride by the amine with formation of a carboxylate anion:



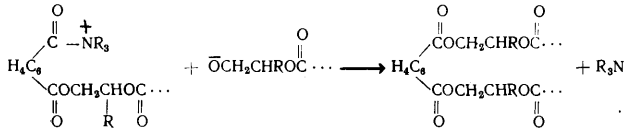
2. Reaction of the carboxylate anion formed with the epoxy-compound to form an alkoxide anion:



3. Reaction of the alkoxide anion with the anhydride:



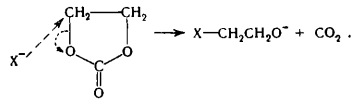
In addition, growth of the polymeric chain is possible also when the amine is replaced by an alkoxide ion:



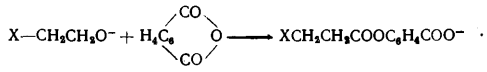
For the preparation of polyesters by the copolymerisation of cyclic compounds, one can use instead of epoxy-compounds the esters of dihydric alcohols and carbonic or sulphurous acids which have a cyclic structure and which are converted at high temperatures into epoxy-compounds with evolution of carbon monoxide or sulphur dioxide[86,87]. In this case polyesters are readily synthesised in the presence of various catalysts (metal oxides, tetraethylammonium bromide, lithium chloride, alkali metal salts of organic and inorganic acids). Schwenk et al.[86] obtained by this method polyesters with molecular weights up to 90 000. The increase of the rate of copolymerisation with the polarity of the reaction medium at various monomer concentrations and also the fact that the initiator anions are incorporated into the polyester macromolecules during copolymerisation, and finally the termination of the growing chain by substances containing active hydrogen ions indicate an anionic copolymerisation mechanism[87]. Schwenk et al.[86] suggest the following mechanism for the formation of polyesters in the copolymerisation of dicarboxylic acid anhydrides with cyclic carbonates in the presence of salts of the type MX.

1. Initiation:

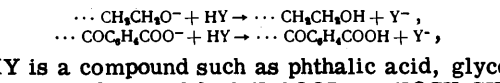
where MX is an alkali metal salt of an organic or inorganic acid;



2. Growth of the polymeric chain:



3. Chain termination:



where HY is a compound such as phthalic acid, glycol, or water and $Y^- = OH^-$, $HOOCC_6H_4COO^-$, or $HOCH_2CH_2O^-$.

Organometallic compounds, for example n-C_4H_9Li, C_2H_5MgBr, $(C_2H_5)_2Mg$, $(C_2H_5)_2Zn$, and $(C_2H_5)_2Cd$ are active catalysts of the reaction of epoxy-compounds with anhydrides[70]. In the presence of diethylzinc the copolymerisation of epoxypropane with anhydrides takes place at relatively low temperatures (about 30 °C). It has been established by infrared spectroscopy and elemental analysis that the copolymer obtained in the copolymerisation of epoxypropane and phthalic anhydride is a polyester with the structural formula $[-CH_2CH(CH_3)OCOC_6H_4COO-]_n$.[70]

Unsaturated polyesters are obtained in the copolymerisation of a mixture of maleic and phthalic anhydrides with epoxypropane in the presence of tetramethyleneammonium bromide or lithium chloride. The polyester formed contains unsaturated bonds and are capable of being modified chemically—for example, it can be copolymerised with styrenes[72].

The copolymerisation of pyromellitic anhydride with the glycidylphenyl ether leads to the formation of a ladder-type polymer in which two polyester chains are linked by bridges consisting of tetrasubstituted benzene rings. The copolymerisation was performed in dioxan in the presence of dimethylbenzylamine, lithium chloride, sodium acetate, sodium phthalate, and triethylaluminium. The first catalyst is the most effective. When the copolymerisation is carried out in dilute solutions, a soluble polyester is formed. Judging from infrared spectroscopic results, the polyester does not contain anhydride groups but its hydrolysis shows that the ratio of the anhydride and epoxy-units is greater than two, i.e. the polymer contains also ester units[73]. The copolymerisation of pyromellitic anhydride with epichlorohydrin and 3,3-bis(chloromethyl)oxetane has also been investigated[73].

The use of an asymmetric catalytic system in the copolymerisation of epoxy-compounds with anhydrides permits the synthesis of active copolymers from inactive monomers. Thus in the copolymerisation of (±)-epoxypropane with the optically inactive 3-phenyl-Δ^4-tetrahydrophthalic anhydride in the presence of the diethylzinc–(+)-borneol system a polyester was obtained which exhibited dextrorotatory optical activity in chloroform (70°).[74]

Branched-chain thermoplastic polyesters are formed in the copolymerisation of dicarboxylic acid anhydrides and epoxy-compounds in the presence of pentaerythritol[88].

4. Other Types of Copolymerisation

Above it was pointed out that epoxy-compounds can undergo copolymerisation with a number of other cyclic monomers (lactones, anhydrides, aziridines), forming copolymers of various types. In addition, there are several patents dealing with the copolymerisation of epoxyalkanes with alkylene sulphides. Alkali metal hydroxides[75] and complexes of $FeCl_2$ and $FeCl_3$ with the monomeric epoxy-compound[77] ($2FeCl_2.C_3H_6O$, $FeCl_3.2C_3H_6O$, and $FeCl_3.3C_3H_6O$) have been suggested as catalysts. In the first case the products are copolymers of low molecular weight (200–1500) which are either mobile liquids or oils. Such copolymers show enhanced stability to oxidation and they are recommended as lubricating oils. In the presence of catalysts of the second type epoxypropane has been copolymerised with phenylethylene sulphide, 1,2-butylene sulphide, and propylene sulphide. Copolymers with a high molecular weight (up to 100 000), capable of forming films stable to the action of light and heat (in the absence of stabilisers) and with a relatively high strength (tensile strength 385 kg cm^{-2}) were obtained.

Tsuruta et al.[77] copolymerised epoxypropane with the *N*-carboxy-anhydride of DL-alanine. Diethylzinc and triethylaluminium are effective catalysts of this copolymerisation. The presence of co-catalysts (water or alcohol) lowers the yield of the copolymer. The main chain of the copolymer obtained probably contains ether, ester, amide, and urethane groups.

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At the present time it can be assumed that generally speaking all heterocycles with sufficiently polar bonds or bonds capable of polarisation under particular conditions can undergo polymerisation. Thermodynamic factors play the main role in carbocyclic compounds. However, the polymerisation conditions have been by no means always discovered and not all cyclic compounds could be polymerised.

Even greater difficulties are encountered in copolymerisation. Even among compounds of the same type, the capacity for polymerisation can differ significantly, which makes copolymerisation difficult. On the other hand, for monomers of different types the determination of copolymerisation conditions is frequently very difficult.

Among the problems which arise in the copolymerisation of cyclic compounds, the following are particularly significant at the present time. Very often the molecular weight of the copolymers is lower than that of the corresponding homopolymers. This can be caused by a difference in the reactivity of the copolymerising compounds, as a result of which the chosen conditions are not altogether suitable for both monomers. The reaction conditions can be too mild for the successful polymerisation of one of the components or too severe, so that one monomer decomposes into substances which inhibit polymerisation. Thus the choice of process conditions is very important. In choosing the conditions for copolymerisation, it is necessary to make sure that they differ as little as possible from the polymerisation conditions of the individual monomers. For this reason the problems of catalysis are of primary importance.

Furthermore, considerable difficulties arise in connection with the very proof that copolymers are formed. In contrast to the copolymerisation of vinyl compounds, in the copolymerisation of monomers of different chemical types it is particularly important to prove the formation of copolymers, since under these conditions the homopolymerisation of one or other monomer takes place readily.

The question of the preparation of block copolymers, particularly those of a regular structure, is of great interest in connection with the copolymerisation of cyclic compounds, as for compounds of other types.

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Metal Ammonium Phosphates and Their New Applications

L.M.Lapina

The review deals with the methods of preparation and applications of double salts comprising metal and ammonium phosphates. Particular attention has been given to the methods of preparation and properties of divalent metal compounds of composition $MNH_4PO_4.nH_2O$ which are interesting as complex, long-acting fertilizers.
The syntheses and investigations of those trivalent metal compounds which can be formed on interaction between water-soluble phosphorus fertilizers and soils are described extensively. The bibliography comprises 65 references.

CONTENTS

I.	Introduction	693
II.	Preparation of compounds of the type $MNH_4PO_4.nH_2O$	694
III.	Properties of compounds of the type $MNH_4PO_4.nH_2O$	695
IV.	Preparation of compounds of the type $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$	697
V.	Properties of compounds of the type $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$	699

I. INTRODUCTION

Metal ammonium phosphates include a wide range of compounds which can be denoted by the common formula $a(NH_4)_2O.bMO.cP_2O_5.nH_2O$, where M is a divalent metal, and $a(NH_4)_2O.M_2O_3.cP_2O_5.nH_2O$, where M is a trivalent metal†.

Many of these compounds were already known in the 19th century. Compounds of the type $MNH_4PO_4.nH_2O$, which have found application in analytical chemistry, have been most thoroughly investigated. For example, the determination of phosphorus and magnesium is based on the isolation of $MgNH_4PO_4.6H_2O$, which is then converted to pyrophosphate by heat treatment, and the isolation of $ZnNH_4PO_4$, $MnNH_4PO_4.H_2O$, and $CdNH_4PO_4.H_2O$ constitutes the basis of the determination of the corresponding metals.

Recently the applications of these compounds have greatly increased. In particular investigators in the field of fertilizers have drawn attention to the fact that certain compounds of the type $MNH_4PO_4.nH_2O$ can be used as complex fertilizers containing three nutrient elements: nitrogen, phosphorus, and the corresponding metal (magnesium, manganese, zinc, copper, etc.). Copper, manganese, and zinc are required by plants in micro-amounts, while magnesium is required in comparatively large quantities.

Technological procedures for the preparation of magnesium, zinc, and iron ammonium phosphates have been developed at the Institute of Fertilizers, Insecticides, and Fungicides (NIUIF).[1] Magnesium ammonium phosphate monohydrate‡ was tested under field conditions on different crops and yielded positive results[2]. Manganese, copper, and zinc ammonium phosphates were subjected to vegetative tests and proved to be fairly effective under many conditions.

American workers showed[3] that the high assimilability of metal ammonium phosphates by plants can be explained by the rapid nitrification of their nitrogen content by soil bacteria, as a result of which the salt molecule breaks down and all the components become available to the plant.

At the beginning of the 1960's Grace and Co. in the USA[4,5] announced the manufacture and application as fertilizers of magnesium ammonium phosphate and certain other similar compounds. This communication was followed by a paper dealing with the study of the properties and tests of these fertilizers[3].

The bright colour of certain of the divalent metal compounds has led to their employment (mainly cobalt ammonium phosphate) as pigments in artists paints[6,7].

Iron ammonium phosphate and manganese ammonium phosphate have been suggested as components of priming paints in anti-corrosion coatings[6,8], since, apart from their other valuable properties, they behave as acceptors of acids and oxygen, whereby they prevent corrosion.

The method of extraction of doubly charged metal cations[9], in particular calcium and magnesium, from sea water to prevent the formation of scale is based on metal ammonium phosphates. In this procedure phosphoric acid and ammonia are added to sea water and the metal ammonium phosphates formed are used as fertilizers.

Salutsky and Dunseth[10] believe it to be more useful to extract cations such as Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, and Ca^{2+} from salt solutions of various types, including sea water, by passing them through a layer of $MgNH_4PO_4.H_2O$, where magnesium ions are replaced by the above cations.

† Compounds in which the ammonium ion is replaced by a monovalent metal (sodium, potassium, lithium) are also very widespread but these will be mentioned only incidentally.

‡ $MgNH_4PO_4.6H_2O$ is of no interest as a fertilizer, since it is unstable and contains a smaller percentage of nutrient substances than $MgNH_4PO_4.H_2O$.

Another valuable property of metal ammonium phosphates is the capacity to decompose in the temperature range 200–400°C (the region of cellulose inflammation) with evolution of ammonia and water and the formation of free phosphoric acid, which makes them suitable as fire-resistant agents.

Attempts have been made to impregnate wood with zinc and copper ammonium phosphates in aqueous ammonia in order to make it fire resistant[11]. Soviet workers suggested[1,12] that iron and aluminium ammonium phosphates be used as fire-resistant agents in the manufacture of non-combustible wood-fibre plates and certain other articles. Industrial methods have been devised for their preparation from readily available raw materials[12,13].

Aluminium and iron ammonium phosphates are formed in the reaction of the soluble fertilizer ammonium phosphates with a number of soils and are responsible for the conversion of water-soluble phosphates into an insoluble form. These studies will be described below. Compounds of aluminium and iron(III) of the type $MM'_3H_{14}(PO_4)_8.4H_2O$, where M = Na, K, or NH_4 and M′ = Fe or Al, have been used as baking powders[14].

Since the applications of metal ammonium phosphates are extremely varied, communications concerning them are published in journals dealing with diverse fields. This review presents a wide variety of information about this large class of compounds.

II. PREPARATION OF COMPOUNDS OF THE TYPE $MNH_4PO_4.nH_2O$

At the present time the following compounds of the above type have been isolated and described: $MgNH_4PO_4.nH_2O$ (n = 1 and 6); $ZnNH_4PO_4$; $FeNH_4PO_4.H_2O$; $MnNH_4PO_4.H_2O$; $CuNH_4PO_4.H_2O$; $CoNH_4PO_4.nH_2O$ (n = 1, 6, and 12); $NiNH_4PO_4.nH_2O$ (n = 1 and 6); $CdNH_4PO_4.H_2O$; $CaNH_4PO_4.nH_2O$ (n = 1 and 7); $BaNH_4PO_4.7H_2O$.

Under normal conditions monohydrates are usually precipitated. Exceptions are magnesium, cobalt, and nickel ammonium phosphates which are isolated as hexahydrates, and also zinc ammonium phosphate which is precipitated in the anhydrous state. Lasne[15] isolated calcium ammonium phosphate as the heptahydrate from a solution of calcium oxide in citric acid on introduction of ammonium phosphate into the latter. This salt is unstable, losing water and ammonia on standing in air.

Auger and Ivanoff[16] obtained $BaNH_4PO_4.7H_2O$ and $CaNH_4PO_4.7H_2O$ in the presence of a large amount of ammonium citrate at a low temperature (0–7°C).

Basset and Bedwell[17] described a general method for the preparation of metal ammonium phosphates. It consists in mixing solutions of the given metal chloride and diammonium hydrogen phosphate in a large excess, the mixture being stirred. The resulting mixture of precipitate and mother liquor is kept at room temperature or on a water bath until the precipitate becomes crystalline. It is then filtered off and washed with water, absolute alcohol, and absolute ether. The concentrations of the solutions for different compounds vary, but are in all cases comparatively low. In the individual methods recommended by Basset and Bedwell the amount of ammonium phosphate is reduced by the addition of a large quantity of ammonium chloride. The crystallisation of the hexahydrates required 12 h and that of monohydrates 1 h, except for copper ammonium phosphate which crystallised very slowly. With the ratio P : Cu ≃ 9, the crystallisation of $CuNH_4PO_4.H_2O$ required three months, while with P : Cu ≃ 40, 24 h was sufficient. Basset and Bedwell obtained by the above method all the compounds enumerated above, with the exception of iron, calcium, and barium ammonium phosphates. The hydrates which could not be isolated, for example the hexahydrates of manganese, copper, zinc, and cadmium ammonium phosphates, were obtained in the form of solid solutions in an excess of magnesium ammonium phosphate hexahydrate. The anhydrous compounds of cobalt and magnesium were obtained in the form of solid solutions in zinc ammonium phosphate. Using dipotassium hydrogen phosphate instead of diammonium hydrogen phosphate, the authors obtained a number of metal potassium phosphates by the method adopted for metal ammonium phosphates in particular $KMgPO_4.H_2O$, $KMnPO_4.H_2O$, $KCoPO_4.H_2O$, $KCuPO_4.H_2O$, $KCdPO_4.H_2O$, $KZnPO_4$, and $KMgPO_4.6H_2O$.

Grat-Cabanac[18] obtained the pure salt $CoNH_4PO_4.H_2O$ at 80°C from dilute $CoSO_4$ and $(NH_4)_2HPO_4$ solutions with a large excess of the latter.

Depending on the temperature (15–95°C), mixtures with different amounts of water of crystallisation were obtained. Frazier et al.[19] determined the amount of calcium ammonium phosphate monohydrate in the products of the ammonia treatment of superphosphate. Apart from $CaNH_4PO_4.H_2O$, two dimorphous salts with the composition $Ca(NH_4)_2.(HPO_4)_2.H_2O$ were found. The authors investigated the four-component system $CaO–P_2O_5–NH_3–H_2O$ at room temperature in the pH range 4–9 and established the regions of existence of these salts. The compounds were obtained in a pure form by adding calcium hydroxide or calcium carbonate to concentrated ammonium phosphate solutions with N : P molar ratios between 1 and 3.4 and at pH between 4.0 and 9.9. Their X-ray diffraction patterns and crystal-optical characteristics were determined.

The four-component system $MgO–P_2O_5–NH_3–H_2O$ was investigated by Abashkina[20] at 25°C in the concentration ranges 2.7–60.97% P_2O_5, 0.07–7.67% MgO, and 0.53–12.40% NH_3 and at 75°C in the concentration ranges 0.2–57.08% P_2O_5, 0.09–11.63% MgO, and 0.22–15.22% NH_3. It was established that the region of crystallisation of magnesium ammonium phosphate is located in the most alkaline part of the diagram both at 25° and at 75°C. At 75°C the stable phase is $MgNH_4PO_4.H_2O$, while at 25°C compounds with different degrees of hydration (between 6 and 1 moles of water per mole of salt) were found, depending on the concentration of phosphorus pentoxide in the liquid phase. This finding is inconsistent with the usual hypotheses, according to which the hexahydrate is precipitated at room temperature.

Much work has been done on the technological methods of preparation of metal ammonium phosphates, particularly magnesium ammonium phosphate, in view of their considerable value as fertilizers. Aseev[21] took out a patent for the simultaneous preparation of magnesium bicarbonate and magnesium ammonium phosphate hexahydrate from magnesium minerals, in particular dolomite. Vol'fkovich and Remen[22] developed a method for the preparation of magnesium ammonium phosphate monohydrate from hot concentrated solutions of magnesium chloride and diammonium hydrogen phosphate, which were neutralised with ammonia to pH 8–8.5 after mixing. The proportions of the reactants were close to the stoichiometric values, the time of reaction being 0.5 h. The precipitate was filtered off, washed with hot water, and dried at 106°C. Magnesium ammonium phosphate forms according to the reaction $MgCl_2 + (NH_4)_2HPO_4 + NH_4OH = MgNH_4PO_4.H_2O\downarrow + 2NH_4Cl$. The carbonate was also tested as the raw material; it was stirred in boiling water and allowed to react with the solu-

tion of monoammonium dihydrogen phosphate without additional neutralisation with ammonia. In both cases a product close to the theoretical composition was obtained.

Erskine et al.[8] synthesised $FeNH_4PO_4.H_2O$ for tests as a component of priming paints composed of a ferrous salt and diammonium hydrogen phosphate at pH 8.5. Vol'fkovich and Remen[1] obtained an experimental batch of this product under industrial conditions. The same workers developed a technological method for the synthesis of zinc ammonium phosphate from zinc or zinc oxide, phosphoric acid, and ammonia, on the basis of the reactions

$$ZnO + H_3PO_4 = ZnHPO_4 + H_2O,$$
$$ZnHPO_4 + NH_3 = ZnNH_4PO_4.$$

Salutsky et al.[23] (Grace and Co.) patented a method for the synthesis of metal ammonium phosphates consisting of the following operations: mixing of phosphoric acid with any compound of the corresponding metal soluble in phosphoric acid; (2) treatment of the mixture at 80–105°C for a period ranging from 10 min to 4 h, which results in the formation of a dimetal hydrogen phosphate salt; (3) introduction of ammonia until the attainment of pH 7–9; (4) treatment of the ammonia-pretreated mixture at 25–105°C for a period ranging from 1 h to several days; (5) washing of the precipitate with water; (6) drying at 65–105°C. They obtained by this method magnesium, iron, manganese, nickel, copper, zinc, and cobalt ammonium phosphates. Somewhat later the same firm[24] took out a patent for a continuous method of synthesis of magnesium, nickel, cobalt, and zinc ammonium phosphates, consisting in the continuous supply of a solution of the salt in phosphoric acid and of ammonia at 75–85°C with the pH in the reaction zone about 7.5; the average residence time was 6–9 min.

This method scarcely differs from the procedures developed earlier for the synthesis of magnesium, iron, and zinc ammonium phosphates. The preparation of the salt of the corresponding metal in phosphoric acid is not obligatory: all the compounds can be readily obtained by the simultaneous introduction of the metal salt, phosphoric acid (or ammonium phosphate), and ammonia. The manufacture of iron ammonium phosphate in the USSR is based on this procedure[12]. Apart from magnesium, zinc, and iron ammonium phosphates, manganese and nickel ammonium phosphates can be obtained by this method. Equilibrium in the system $CuO-P_2O_5-NH_3-H_2O$ is established very slowly and therefore a periodic process is more suitable for the synthesis of $CuNH_4PO_4.H_2O$.

In recent years, apart from American studies, communications from other countries have appeared, dealing with the preparation of metal ammonium phosphates, mainly magnesium ammonium phosphate, and their use as fertilizers. Japanese workers[25] have described a method for the synthesis of magnesium ammonium phosphate from magnesium hydroxide, phosphoric acid, and ammonia and investigated the effect of the atomic ratio N : P on the purity of the product.

Hungarian investigators[26] suggested that calcium hydrogen phosphate and ferrous sulphate be used as the starting materials. In this case gypsum is formed as a by-product. The process consists of three stages. The dihydrogen phosphate formed is neutralised with ammonia and the resulting ammonium dihydrogen phosphate is precipitated with the carbonate, oxide, or hydroxide of one of the divalent metals:

$$Ca(H_2PO_4)_2 + MSO_4 = \downarrow CaSO_4 + M(H_2PO_4)_2,$$
$$M(H_2PO_4)_2 + 2NH_3 + nH_2O = \downarrow MNH_4PO_4 \cdot nH_2O + NH_4H_2PO_4,$$
$$NH_4H_2PO_4 + M'CO_3 + nH_2O = H_2CO_3 + M'NH_4PO_4 \cdot nH_2O.$$

By this procedure, it is possible to obtain a mixed fertilizer containing several microelements by introducing into the first reaction the salt of one element and into the last reaction that of another. In the Research Laboratory of the Budapest Chemical Factory[27] a fertilizer containing microelements was obtained, with magnesium ammonium phosphate as the main substance.

There is a Japanese patent[28] for the synthesis of a complex fertilizer containing magnesium ammonium phosphate.

In the above method metal ammonium phosphates are produced in the form of powders. However, American workers believe[3] that, despite their low solubility, metal ammonium phosphates can be obtained in a granulated form, the rate of assimilation of the nutrient substances by the plants being regulated by the size of the granules. The firm Grace and Co. took out two patents for the synthesis of granulated magnesium ammonium phosphate[29,30].

In technological syntheses the formation of metal ammonium phosphates of definite composition is not achieved by means of a large excess of diammonium hydrogen phosphate but by establishing a strongly alkaline medium with the aid of ammonia. Possibly, under manufacturing conditions completely homogeneous products are not obtained, but their purity is quite satisfactory for technical purposes.

For other compounds of the type $a(NH_4)_2O.bMO.cP_2O_5.nH_2O$, there is early information about zinc ammonium phosphates of the composition $(NH_4)_2O.2ZnO.2P_2O_5.5H_2O$ and $4(NH_4)_2O.6ZnO.3P_2O_5$,[31] and also about the iron ammonium phosphate $(NH_4)_2O.FeO.P_2O_5.5H_2O$.[32]

In connection with the expansion of studies on fertilizers and the synthesis of new types of fertilizers, including those containing magnesium and microelements, the number of compounds of this type which have been isolated has greatly increased in recent years.

Lindsay et al.[33] established the presence of the compound $Ca_2(NH_4)_2(HPO_4)_3.2H_2O$ among the products of the interaction of diammonium hydrogen phosphate with soils.

Much work has been done by Frazier et al.[34] on the identification of the compounds formed when the phosphoric acid extract containing magnesium and microelements is treated with ammonia. In the presence of magnesium in the acid, the compounds $Mg_3(NH_4)_2H_4(PO_4)_4.8H_2O$ [empirical formula $(NH_4)_2O.3MgO.2P_2O_5.10H_2O$], corresponding to the mineral hannayite, and $Mg(NH_4)_2H_2(PO_4)_2.4H_2O$ [$(NH_4)_2O.MgO.P_2O_5.5H_2O$] were isolated in addition to $MgNH_4PO_4.6H_2O$ and the corresponding monohydrate. In the presence of aluminium the salt $MgAl(NH_4)_5H_2(PO_4)_4.6H_2O$ was found.

When phosphoric acid containing zinc was treated with ammonia, the salt $ZnNH_4H_3(PO_4)_2.H_2O$ [empirical formula $(NH_4)_2O.2ZnO.2P_2O_5.5H_2O$], mentioned earlier, was obtained in addition to $ZnNH_4PO_4$, and in the presence of potassium the salts $Zn_2KH(PO_4)_2.2H_2O$ and $ZnKPO_4$ were found.

III. PROPERTIES OF COMPOUNDS OF THE TYPE $MNH_4PO_4.nH_2O$.

1. Solubility

The compounds $MNH_4PO_4.nH_2O$ are crystalline salts sparingly soluble in water, which dissolve readily in mineral acids. The solubility of most of these compounds in water and dilute hydrochloric acid was determined by Bridger et al.[3], who estimated the solubility from the amount of phosphate ions passing into solution, assuming that the compounds dissolve congruently. However, Taylor and Frazier[35], who investigated the solubility of $MgNH_4PO_4.6H_2O$ under equilibrium conditions, established that this

compound dissolves incongruently with precipitation of $Mg_3(PO_4)_2$. From the compositions of the solutions in equilibrium with the solid phase at 25°C, they calculated the solubility product of $MgNH_4PO_4.6H_2O$ as 7.1×10^{-14}. The solubility of magnesium ammonium phosphate increases somewhat in the presence of other salts, especially ammonium salts[36] (with the exception of ammonium phosphate). A similar situation was found with $MnNH_4PO_4.H_2O$.[37] Investigations of this kind were not performed on other salts.

It has been established in a number of studies[2,3,5,38,39] that, despite their low solubility in water, many metal ammonium phosphates give rise to a satisfactory agrochemical effect. Lunt et al.[38] and Munk[39] studied the effect of soil conditions on the assimilability of magnesium ammonium phosphate.

2. Thermal Stability

A number of investigations have shown that the hexahydrates are very unstable—they begin to decompose even at room temperature. The monohydrates are much more stable.

Kiehl and Hardt[40] determined the vapour pressure over $MgNH_4PO_4.6H_2O$ and other compounds which might form in its decomposition. They established that below 60°C only water is lost, while above 60°C ammonia begins to appear in the gas phase with simultaneous evolution of the residual water. At 105°C the vapour pressure over $MgNH_4PO_4.6H_2O$ reaches 1 atm. According to the data of these workers, magnesium ammonium phosphate monohydrate begins to decompose at about 150°C, the vapour pressure reaching 1 atm at 250°C. It was established that, when $MgNH_4PO_4.H_2O$ is heated, ammonia is evolved together with water and that $Mg_2P_2O_7$ is formed at a very low temperature, of the order of 200°C, which can be accounted for by the high vapour pressure over $MgHPO_4$.

Auger and Ivanoff[16] found that, on drying $MgNH_4PO_4.6H_2O$ to constant weight at 55°, 70°, and 100°C, 28%, 42%, and 74% of ammonia relative to the initial amount is lost. Water is liberated together with ammonia; at 55°C the loss amounted to 20% and at 70°C to 82% of the total water content. These results show that magnesium ammonium phosphate monohydrate cannot be obtained from the hexahydrate by heating the latter.

Vol'fkovich et al.[41] investigated the stability of magnesium ammonium phosphate hexahydrate and monohydrate in order to determine how these products would behave on storage when used as fertilizers. They established, that when air is passed over a weighed sample of $MgNH_4PO_4.6H_2O$, a small ammonia loss is observed even at room temperature. The heating curves for $MgNH_4PO_4.6H_2O$ and $MgNH_4PO_4.H_2O$ were determined.

French workers made a systematic study of the thermal decomposition of many metal ammonium phosphates[42-44]. It involved the analysis of the intermediate products by X-rays spectroscopy and chromatography. The monohydrates of beryllium, manganese, magnesium, and cobalt ammonium phosphates were investigated. In addition, the thermal decomposition of $CoNH_4PO_4.6H_2O$ and $CoNH_4PO_4$, obtained by heating the monohydrates in a stream of ammonia at 260°C, was studied. $MgNH_4PO_4.H_2O$ was obtained from the hexahydrate by heating the latter in a stream of ammonia at 110°C. The weight loss was determined by means of a thermobalance, with simultaneous analysis of the gas phase for water and ammonia.

The investigation showed that the decomposition of metal ammonium phosphates on heating proceeds via a series of intermediate compounds. In all cases the presence of an amorphous phase was established in the range 220–650°C. The range of existence of the phase is different for different compounds: for $CoNH_4PO_4.H_2O$, the amorphous phase is present between 390 and 415°C, while for $MgNH_4PO_4.H_2O$, the range of its existence is more extensive (225–650°C). Acid phosphates were not detected among the decomposition products, in agreement with the data of Kiehl and Hardt[40].

As a rule, the decomposition of the monohydrates begins at 150–200°C with evolution of water. Sometimes ammonia is liberated together with water. The evolution of water and ammonia takes place in several stages. The final products of the thermal decomposition are pyrophosphates. A simplified decomposition mechanism can be represented thus:

$$MNH_4PO_4 \cdot H_2O \xrightarrow{-NH_3-H_2O} \text{amorph. phase} \xrightarrow{-NH_3-H_2O} M_2P_2O_7 .$$

Ortho-, pyro-, and tri-phosphate ions were detected in the amorphous phase by chromatography. However, none of the intermediates was isolated in a pure form, since several processes superimposed upon one another take place in the decomposition. Traces of orthophosphate were detected even at 580°C, while the more dehydrated form (pyrophosphate) is sometimes observed at a temperature as low as 200°C.

The pyrolysis of $CoNH_4PO_4.6H_2O$ begins at 85°C. It resembles the decomposition of the monohydrates. The decomposition of anhydrous cobalt ammonium phosphate, which was first investigated by Etienne and Boulle[44], begins at 230°C and is also accompanied by the evolution of ammonia and water.

The above investigations show that the decomposition of metal ammonium phosphates is such that it is impossible to distinguish between the evolution of the water of crystallisation and the water of constitution. Hence one may conclude that these compounds have a more complex structure than might be expected from the formula $MNH_4PO_4.nH_2O$ attributed to them.

3. The Structure of Compounds of the Type $MNH_4PO_4.nH_2O$

Structural studies on compounds of the type $MNH_4PO_4.nH_2O$ are not recorded in the literature. Certain hypotheses have been put forward on the basis of their unusual behaviour on heating and the colour changes in the precipitation of coloured salts, mainly cobalt ammonium phosphate.

As early as the 19th century, it was noted that some of these compounds glow on heating. Basset and Bedwell[17] established that the intensity of the glow of the hexahydrates is greater than that of the monohydrates. On this basis, they concluded that the monohydrates are polymeric compounds, while the hexahydrates polymerise during heating and that this process is responsible for the luminescence.

Many investigators drew attention to the fact that the precipitation of $CoNH_4PO_4.H_2O$ is accompanied by a number of colour changes in the precipitate. Initially a pink flaky precipitate is deposited, which then assumes a bright blue colour, and is finally transformed into the violet-red monohydrate. Golynkin[6] and Grat-Cabanac[18] explained this by the initial formation of more hydrated forms, while Basset and Bedwell[17] concluded that the intermediate bright blue compound is anhydrous cobalt ammonium phosphate. Since the hexahydrates have a pure colour (pink for $CoNH_4PO_4.6H_2O$ and green for $NiNH_4PO_4.6H_2O$) corresponding to the colour of the hydrated cation, while the monohydrates assume also another tint, Basset and Bedwell concluded that

in the hexahydrates the metal is present in the cationic form and in the monohydrates partly in the cationic and partly in the anionic forms. Bearing this in mind and also the fact of a higher degree of polymerisation of the monohydrate which they established and the coordination numbers of the metals, they assigned to the hexahydrates the formula

$$NH_4^+ [M(H_2O)_6]^{3+} PO_4^{3-},$$

and to the monohydrates

$$(NH_4^+)_2 [M(H_2O)_4]^{2+} (PO_4MPO_4MPO_4MPO_4)^{6-}.$$

Evidently these formulae too fail to reflect the true structure of compounds of the type $MNH_4PO_4.nH_2O$. According to them, ammonia should be evolved first on heating. They do not explain why water and ammonia are evolved in several stages, suggesting that the bond between the metal and both water and ammonia is the same. More detailed studies in this field were not made and therefore the problem of the structure of these compounds still remains unresolved.

IV. PREPARATION OF COMPOUNDS OF THE TYPE $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

Compounds of this type, whose composition corresponds to the formula $(NH_4)_2O.(Al,Fe)_2O_3.2P_2O_5.2H_2O$, were obtained for the first time by Cohen[45] by mixing a concentrated solution of diammonium hydrogen phosphate and a solution of aluminium chloride (or ferric chloride) in hydrochloric acid in the presence of a large excess of phosphate ions ($PO_4 : Al = 23$, $PO_4 : Fe = 7$) and with prolonged heating. Somewhat later an iron salt of this composition was obtained by Weinland and Ensgraber[46] from freshly precipitated ferric hydroxide, phosphoric acid, and ammonia. It differed from Cohen's salt in its colour: Cohen's salt was white and Weinland's salt was pink.

The authors investigated it under the microscope and established that it consists of crystals comprising hexagonal rods narrowing at one end. Both Cohen and Weinland and Ensgraber suggested that this compound can be regarded as the ammonium salt of diphosphatoferric(III) acid, which they called "ammonium diphosphatoferrate", and assigned to it the formula $[Fe(PO_4)_2]H_2NH_4$. Apart from this salt, they obtained other compounds, to which they assigned the formulae $[Fe(PO_4)_2H_3]_3.NH_3.7H_2O$ [empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.22H_2O$] and $2FePO_4.NH_3.4H_2O$ [empirical formula $(NH_4)_2O.2Fe_2O_3.2P_2O_5.7H_2O$], and also a salt with the ratios $Fe : PO_4 : N = 4 : 9 : 1.5$, which they regarded as the ammonium salt of di- and tri-phosphatoferric(III) acid $H_6Fe(PO_4)_3$. The salts obtained did not dissolve in water but dissolved readily in dilute hydrochloric acid and more slowly in nitric acid. They were decomposed by alkalis with formation of ferric hydroxide and ammonium phosphate. The solubility of $2FePO_4.NH_3.4H_2O$ is lower than that of the remaining salts.

Many investigators[47-49] failed to prepare ammonium aluminophosphate, described by Cohen, using his procedure. Yakimach[47] obtained a salt of this composition but by a procedure differing from that of Cohen: the precipitation was carried out at a higher concentration of phosphate ions and in the absence of hydrochloric acid. In contrast to Cohen's salt, that synthesised by Yakimach did not dissolve in acids. In the author's view this salt had nothing in common with Cohen's salt.

Angelescu and Balanescu[50] studied the composition of the precipitate deposited from solutions containing Fe^{3+} and PO_4^{3-} ions in the presence of different amounts of ammonia. They established that ferric phosphates of definite compositions can be obtained from acid solutions, but in alkaline solutions "adsorption complexes" are formed, whose composition varies with concentration, temperature, etc.

The composition of the insoluble products formed in the synthesis of ammonium phosphates from a phosphate starting material containing aluminium and iron was investigated at the Institute of Fertilizers, Insecticides, and Fungicides (NIUIF). At pH 4.5 and 3.5 for the aluminium salt and at pH 2.5 for the ferric salt in the presence of a large excess of phosphate ions ($PO_4 : Al = 13$; $PO_4 : Fe = 7.5$), Sannikova[51] obtained salts whose compositions were comparatively close to those of Cohen's salts. The salts were precipitated by mixing together at 45°C solutions of the hydroxide in phosphoric acid and of aqueous ammonia followed by prolonged exposure of the resulting precipitate to this temperature. The salts thus prepared were sparingly soluble in water, more so in 2% citric acid, and completely soluble in a solution of ammonium citrate neutralised with ammonia to pH 8 (Peterman's solution). Using a similar procedure, Kheifets[52] obtained at pH 4.8 a yellow-green salt, close in composition to the salt $2FePO_4.NH_3.4H_2O$ described by Weinland and Ensgraber[46], and at pH 1.7 she obtained a lilac-pink preparation similar to the salt $[Fe(PO_4)_2H_3]_3NH_3.7H_2O$. A product approaching the composition of $Fe(PO_4)_2H_2NH_4$, but nevertheless differing from the latter appreciably, was obtained at pH 3.8. The form of the crystals obtained by Kheifets differed as a rule from that of the salts described by Weinland and Ensgraber.

The results of different investigators show that the composition and properties of the precipitates deposited from solutions containing phosphate ions and the corresponding metal and ammonium ions depend to a high degree on the precipitation conditions. This has been confirmed by a study[53] where precipitates of different compositions were obtained by varying the concentration of the solutions, the pH of the medium, or the proportions of the reactants.

Haseman et al.[54] isolated a number of ammonium and potassium phosphato-ferrates(III) and -aluminates from dilute solutions under conditions imitating those obtaining in soils, namely by prolonged storage in a sealed vessel of precipitated aluminium and ferric phosphates with solutions containing potassium and ammonium cations. Solutions of various concentrations, ranging from 0.001 M to 3.5 M, and at various pH between 1.5 and 8 were prepared by adding potassium hydroxide or ammonium hydroxide to standard phosphoric acid solutions. The precipitates were treated at temperatures between 27° and 145°C. The filtered and washed precipitates were dried at room temperature over calcium chloride.

Each specimen obtained was studied under the petrographic microscope and the optical properties of the crystals were determined. Almost all the products were well crystallised. The aluminium phosphates contained as a rule only one mineralogical variety, while certain of the ferric phosphate specimens contained two or more mineral types; in this case a relatively pure specimen was obtained by screening or elutriation. Homogeneous specimens were analysed chemically and their powder diffraction patterns were obtained.

On the basis of the diffraction patterns, crystal-optical properties, and chemical composition, Haseman classified all the specimens into nine groups of minerals, which are listed in Table 1. Each group is characterised by definite chemical composition, diffraction patterns, and crystal-

optical properties. The authors identified compounds of group 1 with the natural mineral taranakite. They also obtained the analogous ammonium compound. Smith and Brown[55], who investigated this compound by X-ray diffraction, concluded that it is more correct to assign to it the formula $3(NH_4)_2O.5Al_2O_3.8P_2O_5.42H_2O$ or, in an expanded form, $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$.

Table 1. Empirical formulae and the classification of phosphatoferrate and phosphatoaluminate minerals (according to Haseman et al.[54]).

Product	Empirical formula	Classification group
A	$2K_2O\cdot3Al_2O_3\cdot5P_2O_5\cdot26H_2O$	1
B	$2K_2O\cdot3Al_2O_3\cdot5P_2O_5\cdot20H_2O$	1
C	$K_2O\cdot Al_2O_3\cdot2P_2O_5\cdot4H_2O$	2
D	$K_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot4H_2O$	2
E	$K_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot2H_2O$	3
F	$(NH_4)_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot3H_2O$	3
G	$(NH_4)_2O\cdot Al_2O_3\cdot2P_2O_5\cdot3H_2O$	3
H	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot5H_2O$	4
HH	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot5H_2O$	4
I	$K_2O\cdot2Fe_2O_3\cdot2P_2O_5\cdot5H_2O$	4
J	$(NH_4)_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot6H_2O$	4
K	$(NH_4)_2O\cdot3Fe_2O_3\cdot6P_2O_5\cdot20H_2O$	5
L	$K_2O\cdot3Fe_2O_3\cdot6P_2O_5\cdot20H_2O$	5
MM	$Al_2O_3\cdot P_2O_5\cdot4H_2O$	6
O	$0.9Fe_2O_3\cdot0.1Al_2O_3\cdot P_2O_5\cdot4H_2O$	6
P	$Fe_2O_3\cdot P_2O_5\cdot4H_2O$	6
Q	$Al_2O_3\cdot P_2O_5$	7
R	$K_2O\cdot Al_2O_3\cdot P_2O_5\cdot4H_2O$	8
S	$K_2O\cdot Al_2O_3\cdot P_2O_5\cdot2H_2O$	8
T	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot1.6HF\cdot6.2H_2O$	9

Lindsay et al.[33] identified 30 crystalline phosphates (apart from the amorphous precipitates) formed in the reaction between phosphate fertilizers and soils. They investigated the reaction of calcium hydrogen phosphate, ammonium dihydrogen phosphate, potassium dihydrogen phosphate, diammonium hydrogen phosphate, dipotassium hydrogen phosphate, and liquid ammonium-treated superphosphoric acid of type 11-33-0 with sandy and rich calcareous loams. Part of the compounds isolated, relevant to the present review, are listed in Table 2, which shows that the authors obtained ammonium and potassium taranakites and also compounds corresponding to products K, L, P and F in Haseman's classification, but the last product had a somewhat lower water content. The component ratio in the compound $NH_4Al_2(PO_4)_2OH.8H_2O$ corresponds to Haseman's product J but contains a much greater amount of water.

The salts obtained by Cohen and one of Weinland's salts correspond in their chemical composition to compounds or group 3§ (Table 2). However, the ammonium phosphatoferrate(III) described by Weinland consisted of pink crystals comprising hexagonal rods narrowing at one end, while Haseman's product consisted of colourless plates, i.e. the structures of the salts were different.

The present author obtained[53] from concentrated solutions of pH 5 a salt similar in composition to $(NH_4)_2O.Al_2O_3.2P_2O_5.3H_2O$ investigated by Haseman, but their powder diffraction patterns had nothing in common.

Unfortunately the system $(NH_4)_2O-Al_2O_3(Fe_2O_3)-P_2O_5-H_2O$ was not investigated in detail and therefore it is difficult to say whether the various properties of salts of the same composition are due to the fact that some investigators obtained metastable or contaminated compounds or whether it is due to the fact that there exists such a wide variety of compounds in this system at a small change in conditions leads to the formation of a new salt.

Tables 1 and 2 show that a considerable amount of ammonium phosphato-ferrates(III) and -aluminates was also isolated from dilute solutions. Some of these were obtained by many investigators and are well known. For example, there is no doubt that the reaction of ammonium phosphate with many soils results in the formation of a compound whose composition and properties correspond to the mineral taranakite. Such a compound was found by Lindsay[33] in the product of the reaction of calcium hydrogen and ammonium dihydrogen phosphates with sandy and rich calcareous loams. It was also obtained by Tamimi et al.[56] by the reaction of ammonium phosphate at pH 1.0–5.0 with gibbsite $[Al(OH)_3.3H_2O]$ and certain other soils. The same compound was prepared by Haseman in the reaction of aluminium phosphate with dilute solutions (between 0.001 and 1 M) of ammonium phosphate at pH between 1.7 and 5.5. Ammonium and potassium taranakites were also prepared by Taylor and coworkers[57–60], Egan et al.[61], Arlidge et al.[62], and, as already stated, Smith and Brown[55]. Lindsay and Taylor[58] investigated the assimilability of taranakite by plants.

Compounds of group 3 (according to Haseman's classification) were prepared by Lindsay[33] (iron derivatives) and Smith and Brown[55] (aluminium derivatives) and those of group 5 by the same authors and Arlidge et al.[62] However, the compound $NH_4Fe_3H_6(PO_4)_6.6H_2O$ differed in its X-ray diffraction characteristics from the compound described by Haseman.

§ Cohen's compounds contained a lower percentage of water, but this can be attributed to the inaccuracy of the determination, since it was found by difference.

Table 2. Phosphatoaluminates and phosphatoferrates(III) identified in the products of the reaction of phosphate fertilizers with soil[33].

No.	Chemical formula	Empirical formula	Mineral	Form of phosphate fertilizer
1	(K, H) (Fe, Al)$_3$H$_6$(PO$_4$)$_6$·6H$_2$O	$K_2O(H_2O)3Fe_2O_3(Al_2O_3)\cdot6P_2O_5\cdot20H_2O$		$Ca(H_2PO_4)_2$
2	(NH$_4$, H) (Fe, Al)$_3$H$_6$(PO$_4$)$_6$6H$_2$O	$(NH_4)_2O(H_2O)\cdot3Fe_2O_3(Al_2O_3)\cdot6P_2O_5\cdot20H_2O$		ditto
3	Colloidal (Fe, Al)PO$_4$·n H$_2$O			$Ca(H_2PO_4)_2$; $NH_4H_2PO_4$, $(NH_4)_2HPO_4$
4	FePO$_4$·2H$_2$O	$Fe_2O_3P_2O_5\cdot4H_2O$	strengite	Ca $(H_2PO_4)_2$
5	FePO$_4$·2H$_2$O	ditto	metastrengite	ditto
6	K$_3$Al$_3$H$_8$(PO$_4$)$_8$·18H$_2$O	$3K_2O\cdot5Al_2O_3\cdot8P_2O_5\cdot42H_2O$	K-taranakite	$Ca(H_2PO_4)_2$; KH_2PO_4
7	(NH$_4$)$_3$Al$_5$H$_6$(PO$_4$)$_8$·18H$_2$O	$3(NH_4)_2O\cdot5Al_2O_3\cdot8P_2O_5\cdot42H_2O$	NH_4-taranakite	$Ca(H_2PO_4)_2$; $NH_4H_2PO_4$
8	NH$_4$Fe(HPO$_4$)$_2$	$(NH_4)_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot2H_2O$		$NH_4H_2PO_4$
9	NH$_4$Al$_2$(PO$_4$)$_2$OH·8H$_2$O	$(NH_4)_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot17H_2O$		$(NH_4)_2HPO_4$

Tables 1 and 2 do not exhaust the wide variety of compounds which can be prepared from dilute solutions. In the study of the reaction of ammonium phosphate with gibbsite at a pH in excess of 5.4, Taylor et al.[57] found the following compounds which had not been described earlier: $(NH_4)_2AlH(PO_4)_2.4H_2O$ [empirical formula $2(NH_4)_2O.Al_2O_3.2P_2O_5.9H_2O$] and $NH_4AlPO_4(OH).2H_2O$ [or $(NH_4)_2O.Al_2O_3.P_2O_5.5H_2O$]. Somewhat later the presence of the same compound was established in the precipitate deposited in the reaction of wet-process phosphoric acid with ammonia[34]. The above salts were also prepared artificially by Frazier and Taylor[60]. The composition of the salts is close to that of potassium phosphatoaluminate (product of R of group 8), differing from the latter only in a higher water content, which can be attributed either to an error in its determination or to the capacity of these compounds to form numerous hydrates.

Arlidge et al.[62] obtained the ammonium derivatives $NH_4Fe_2(PO_4)_2.(OH).2H_2O$ corresponding to the mineral leucophosphite (product I, group 4).

In future the above list will probably be extended.

V. PROPERTIES OF COMPOUNDS OF THE TYPE $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

As already mentioned, Haseman et al.[54] investigated in fair detail the compounds synthesised, including certain metal ammonium phosphates.

In recent years much attention has been devoted to the study of the physicochemical properties of taranakite and certain other products of the reaction of soluble phosphates with soils. Taylor and Gurney[59] determined the solubility of the synthetic taranakites $H_6K_3Al_5(PO_4)_8.18H_2O$ and $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$. Their solubility products were calculated from the compositions of the solutions in equilibrium with the solid phase. The negative logarithm of the solubility product of ammonium taranakite was found to be 175.5. This value is regarded as approximate, since account was not taken of the possibility of the formation of complex ions in the liquid phase.

It has been established that, in solutions where the activity product $a_{Al}a_{PO_4}$ exceeds 1×10^{-20}, taranakite dissolves incongruently with formation of amorphous aluminium phosphate.

Egan et al.[61] gave the heat capacities, entropies, and enthalpies of taranakite over a wide range of temperatures, between 10° and 310°K. The entropy at 298.16°K, the enthalpy, and the heat of formation from the elements of $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$ are respectively 339.9 ± 0.6 e.u., 57 170 cal $mole^{-1}$, and −4432 kcal $mole^{-1}$.

Smith and Brown[55] determined by X-ray diffraction analysis the lattice constants and densities of the compounds $(NH_4)_2O.Al_2O_3.2P_2O_5.3H_2O$ (item D, group 3), $(NH_4)_2O.3Fe_2O_3.6P_2O_5.20H_2O$ (product K, group 5), $(NH_4)_2O.3Al_2O_3.6P_2O_5.20H_2O$, and a series of potassium compounds.

Arlidge et al.[62] recorded the powder diffraction patterns and infrared spectra of a large number of synthetic aluminium and iron phosphates corresponding to the natural minerals variscite and metavariscite ($AlPO_4.2H_2O$), strengite and phosphosiderite ($FePO_4.2H_2O$), barrandite (Al, Fe)$PO_4.2H_2O$, leucophosphites (K, NH_4)$Fe_2(PO_4)_2(OH).2H_2O$, and taranakites, and also some of the synthetic phosphates, namely $NH_4Fe_3H_8(PO_4)_6.6H_2O$ [empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.20H_2O$], and the corresponding potassium compound.

The powder diffraction pattern of the salt $NH_4Fe_3H_8(PO_4)_6.6H_2O$ was also recorded by Haseman, but comparison of the two patterns proves them to be completely different.

The products enumerated above were also analysed thermographically.

Frazier and Taylor[60] made optical, X-ray diffraction, and thermographic studies of the artificial taranakites, and the salts $(NH_4)_2.AlH(PO_4)_2.4H_2O$, $NH_4AlPO_4OH.2H_2O$, and $NH_4AlPO_4.OH.3H_2O$ and measured the infrared spectra. Their differential heating curve for ammonium taranakite differed from those obtained by Arlidge et al. and depended on the conditions of the thermographic experiments (in a stream of air or in a stationary atmosphere) and on the dilution of the specimen; on this basis, the authors concluded that thermal analysis is unsuitable for the identification of ammonium phosphatoaluminates.

The ammonium phosphato-ferrates(III) and -aluminates investigated by the present author[53] behaved on heating similarly to the corresponding divalent metal compounds, namely ammonia and water were evolved from the salts in several stages with formation of a series of intermediate compounds, as shown by the changes in the refractive indices and in the colour of the iron compounds. The intermediate compounds were not identified.

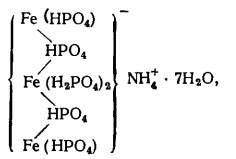
The Structure of Compounds of the Type $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

The application of X-ray diffraction and infrared spectroscopy in the study of certain trivalent metal ammonium phosphates isolated in a pure form established the presence of definite groups in these compounds and demonstrated their distribution, and conclusions concerning their structure were arrived at on this basis. As already stated, Smith and Brown[55], having determined by X-ray diffraction the space groups and the density of the compound $2(NH_4)_2O.3Al_2O_3.5P_2O_5.26H_2O$ obtained by Haseman and corresponding to the natural mineral taranakite, found that the formula $(NH_4)_3Al_5H_6(PO_4)_8.18H_2O$ gives a better representation of the properties of this compound.

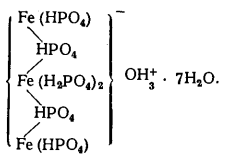
The infrared spectra of taranakite, obtained by Arlidge et al.[62], showed that it contains acid phosphate groups. Arlidge et al. isolated from dilute solutions the compounds $(NH_4, K)_2O.2Fe_2O_3.2P_2O_5.5H_2O$, corresponding to group 4 in Haseman's classification, and found by infrared spectroscopy that they contain the OH and PO_4 groups and water of hydration, which led to their identification with the natural mineral leucophosphite $NH_4Fe_2(PO_4)_2(OH).2H_2O$.

Shishkin and coworkers[63,64], who studied the structure of iron phosphates, established that in some of these part of the water of crystallisation is of the oxonium type. For example, they regard phosphatoferric(III) acid as the oxonium salt $[Fe(HPO_4)_2]^-OH_3^+$, and Weinland's pink salt as an isomorphous compound, and therefore they believe that Weinland's salt is more correctly represented by the formula $[Fe(HPO_4)_2]^-NH_4^+$. They believe that the validity of this formula is confirmed by the fact that two of the hydrogen ions in this salt cannot be substituted by ammonium ions. Furthermore, the compounds $[(Fe(HPO_4)_2]NH_4$ and $[Fe(HPO_4)_2]H_3O$ proved to be very similar in their physical properties (specific gravity, refractive index). It is quite possible that this formula does indeed represent better the structure of the above ammonium phosphatoferrate(III). The possibility of the existence of the complex $[Fe(HPO_4)_2]^-$ in solutions of iron salts in phosphoric acid has been pointed out by Salmon[65].

The second of Weinland's salts, with the empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.22H_2O$, Shishkin and coworkers represent as follows:



believing it to be isomorphous with the phosphate $3Fe_2O_3.6P_2O_5.25H_2O$ or



The review of the literature data shows that, despite the fact that metal ammonium phosphates are already used in various branches of the national economy, their properties and specially their structure have been investigated quite inadequately.

The structure of certain trivalent metal compounds, formed in the reaction between fertilizers and soils, has been investigated more completely using new research techniques (X-ray diffraction, the crystal-optical method, infrared spectroscopy). These studies were stimulated by the requirements of the technology of fertilizers and agrochemistry: the manufacture of new types of fertilizers and the endeavour to improve their efficacy. As already stated, many of these compounds have been prepared artificially from dilute solutions containing aluminium or ferric phosphates and ammonium phosphate. In this concentration range compounds with the same composition and properties were not always obtained.

The situation is even less clear in the range of high concentrations. Among all the compounds obtained, only the existence of the salt $NH_4Fe(HPO_4)_2$ has been firmly established. The information about all other compounds is contradictory.

On the other hand, the divalent metal compounds are readily precipitated from both dilute and concentrated solutions in the form of crystalline salts having definite composition, but here too very little is so far known about their structure; the available information is insufficient for the solution of a number of problems associated with their properties.

In technological processes involving the synthesis of metal ammonium phosphates it is desirable to carry out the precipitation from concentrated solutions and therefore compounds precipitated in this concentration range are of great practical interest. The synthesis of iron ammonium phosphate has already been achieved in the USSR and the synthesis of a fire-resistent agent based on ammonium phosphato-aluminate and -ferrate(III) is being introduced. The necessity to use in the manufacture of fertilizers low-grade phosphorites containing a considerable amount of iron and aluminium has also stimulated the expansion of studies in this field.

The development of studies on the application of a number of metal ammonium phosphates as slowly hydrolysable complex fertilizers containing both macro- and micro-elements and the development of synthetic methods for these compounds are of considerable interest.

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Separation of Rare-earth Elements† by Electrolysis at a Mercury Cathode

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The review deals with the questions of the mechanism of the reduction of rare-earth elements at a stationary mercury cathode and the conditions of their electrochemical deposition and separation, and of their extraction by alkali metal amalgams, are described and discussed. Examples of the separation of almost all the rare-earth elements at a mercury cathode are quoted. The bibliography incorporates 103 references.

CONTENTS

I. Introduction 701
II. Application of the mercury cathode 701
III. Mechanism of the reduction of rare-earth elements 703
IV. Separation of rare-earth elements 705
1. Conditions of electrochemical separation 705
2. Examples of the separation of certain rare-earth elements 708

I. INTRODUCTION

Among the methods for the separation of rare-earth elements available at the present time the most widely used are fractionation based on the gradual variation of the solubility or basicity of rare-earth compounds, ion-exchange and partition chromatography, extraction methods, and electrolysis at a mercury cathode. The last makes it possible, in particular, to separate comparatively readily large amounts of one rare earth from very small amounts of other adjacent elements and can be used in most cases where the separation of large amounts of a rare earth by ion-exchange or fractionation methods involves considerable difficulties.

† Lanthanides is the term used at present in Western literature (Ed.of Translation).

At the present time a large amount of data on the separation of rare earth at a stationary mercury cathode has accumulated. However, unfortunately studies on electrolysis with a mercury cathode for the separation of rare-earth elements has not been reviewed so far. Some information is given in the review of Ryabchikov and Terent'eva[1].

II. APPLICATION OF THE MERCURY CATHODE

The method of the electrolytic reduction of rare-earth elements developed as a result of several studies carried out with different aims. In 1906 Matignon[2] isolated samarium(II) sulphate and in 1911 Urbain and Burion[3] isolated for the first time a europium(II) compound. In

1929 Klemm[4] gave a theoretical explanation of the "anomalous" valencies of the rare earths on the basis of Hund's spectroscopic investigations[5] and theories concerning the structure of rare-earth atoms, and demonstrated the existence of divalent ytterbium. At the present time the "anomalous" properties of rare-earth elements have been fairly adequately elucidated in a series of monographs[6-8].

Studies on the electrolysis of aqueous rare-earth solutions have served as a basis for the development of the method of their electrolytic reduction. Krüss[9] showed that in the electrolysis of aqueous rare-earth chloride solutions with platinum electrodes hydrochloric acid decomposes with the evolution of gaseous chlorine at the anode and of hydrogen and rare-earth hydroxides at the cathode. The decrease of the acidity of the solution observed in this process was subsequently used[10-15] for the separation of rare-earth mixtures by the fractional precipitation of their hydroxides or basic salts.

Yntema[16] replaced the platinum cathode by a mercury cathode and, by virtue of the high hydrogen overvoltage of mercury, achieved the reduction of europium and samarium to the divalent state in a mixture of their chlorides and gadolinium chloride. The divalent state of europium was stabilised by its precipitation as the sparingly solubles sulphate by a small amount of sulphuric acid. Ytterbium was isolated similarly[17]. Prandtl[18] suggested that the electrolysis be carried out directly in rare-earth sulphate solutions but the method used to stabilise the divalent ions in all the studies of this period[19-21] was the same. Electrolytic reduction of rare-earths in the presence of SO_4^{2-} ions gives a relatively low yield of the reduced element and cannot be used to obtain pure preparations of samarium and particularly of other rare-earth elements which do not have a stable divalent state.

A new development in studies in this field was begun by the work of Biltz and Mayer[21], who observed that metallic cerium dissolves in mercury with formation of an amalgam. This suggested the possibility of the preparation of other rare earths by electrolysis with a mercury cathode both in aqueous and in alcoholic solutions[22-25]. However, the electrolytic preparation of rare-earth amalgams is prevented by their precipitation as hydroxides (or basic salts) in the electrolysis of neutral or weakly alkaline solutions. This difficulty was overcome by McCoy[26,27], who suggested that the electrolysis be carried out in weakly alkaline solutions of organic acids (citric and tartaric), from which rare-earth hydroxides in the trivalent state are not precipitated. Under these conditions, rare earths from complexes with the acids, which have been thoroughly investigated and are widely used in analytical practice[28-33].

The method of electrolytic preparation of rare-earth amalgams, in contrast to the electrolytic reduction of rare earths in the presence of sulphate ions, excludes the possibility of the entrainment of the electrolyte solution (occlusion and sorption on the surface) and can yield pure preparations in a single operation. Furthermore, it is possible to select the conditions of electrolysis in such a way that almost all the rare earths can be deposited at a mercury cathode. Using Marsh's experimental data[24], Ryabchikov et al.[35] investigated in detail the effect of different factors on the deposition of ytterbium and increased the degree of its isolation to 93–98%, compared with 23% obtained by McCoy[26]. The electrolysis was carried out at 5°C, pH 6, cathodic current density 25 mA cm^{-2}, ytterbium concentration 0.5–1.0%, and molar ratio $Yb^{3+} : Cit^{3-} = 1 : 2$.

Onstott[36,37] succeeded in separating ytterbium quantitatively (99.98%) from solutions of heavy rare earths by increasing the duration of electrolysis to 8 h and by replacing the potassium amalgam by the lithium amalgam.

Europium was isolated under approximately the same conditions[38-43]. Shvedov and Fu I-pei[41-43] paid particular attention to the effect of the ligand and the alkali metal in the electrolyte as well as the pH of the solution on the degree of isolation of europium. They established that the rate of deposition increases in the sequence Trilon B [sodium salt of EDTA (Ed. of Translation)] > citric acid > > tartaric acid > succinic acid at pH 7.0, 6.8, 9.0, and 9.5 respectively. The yield of europium increases also on raising the current density, the temperature (to 30–40°C), and the pH of the solution (from 4.2 to 9.0 for citrate solutions) and on replacing the alkali metal in the sequence sodium < caesium < potassium < lithium.

Much work has been done on the electrolytic isolation of samarium[26,44-50]. The electrolysis was usually carried out[48] in a vessel similar to a separating funnel (Fig. 1) and fitted with a cooling jacket, a two-way tap, and a balancing flask designed to facilitate the renewal of mercury; the volume of solution was 10 ml, the pH was 6, the potential 8–12 V, and the initial current density 50–100 mA cm^{-2}. The electrolyte and mercury were mixed.

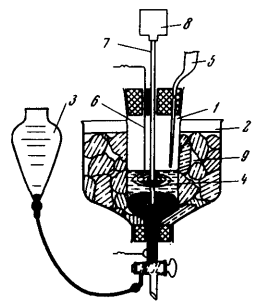

Figure 1. Apparatus for electrolysis with a mercury cathode[48]: *1*) electrolytic cell; *2*) cooling jacket; *3*) balancing flask with mercury serving as the cathode; *4*) initial solution; *5*) tube for the introduction of solution; *6*) platinum anode; *7*) stirrer; *8*) motor; *9*) mixture of dry ice and water.

For example, it was established that the degree of deposition of samarium increases with increasing current density, area of the cathode, the amount of mercury (and its renewal), and duration of electrolysis, and also when potassium ions are replaced by lithium ions; it decreases on raising the concentration of samarium (up to a certain limit) and its content in the amalgam[47-49].

It is interesting to note that the degree of transfer of samarium to mercury at a constant concentration of complex-forming ligand ($Sm^{3+} : CH_3COO^- : Cit^{3-} = 1 : 1 : 2$) is almost constant in the Sm^{3+}-concentration range 6×10^{-3}–6×10^{-2} M, amounting to about 95%. At low concentrations (10^{-4}–10^{-6} M) the degree of its isolation is also high and constant even when the ratio $Sm^{3+} : Cit^{3-}$ is increased by a factor of 5000.

The conditions for the isolation of samarium, europium, and ytterbium in the form of amalgams by the electrolysis of their solutions containing complex-forming ligands (Table 1) were used also for the investigation of the behaviour of other rare earths at the mercury cathodes.

The isolation of promethium was first mentioned by Nauman and Heyne[45] and the conditions for the isolation of this element and other rare earths were investigated in detail in subsequent studies[42,47-53]. The optimum conditions for the isolation of certain rare earths are given in Table 2.

Table 1. Optimum conditions for the electrolytic reduction of ytterbium, samarium, and europium at a mercury cathode.

Rare earth	Cathodic current density, mA cm^{-2}	pH of medium	Type of amalgam	Temp., °C	Molar ratio Ln_2O:Cit^{3-}	Concn. of Ln_2O_3,%	Duration of electrolysis, min	Yield,%	Refs.
Yb	50	6,0	K	+5	1:2	1.5—2	60	93.2	35
Sm	100	5.8—6.0	K, Li	0—2	1:2.3	1.8	60	97.2	49
								99.7	47
Eu + Sm	12.6	8.4	Li	+20; +25	1:1.5	2.3	240	99.8	39
Eu	4.2	7.0	Li	+18	1:14	0.12	25	98.1	41
Eu	50	6.6	K	0—2	1:2	3.7—4.2	60	97.1	44

Table 2. Isolation of rare-earth elements (without a stable divalent state) by electrolysis at a mercury cathode (volume of electrolyte 10–25 ml; $c_{Ln^{3+}}$ between 10^{-7} and 10^{-8} M).

Rare earth	Optimum conditions for isolation						Refs.
	cathodic current density, mA cm^{-2}	pH of soln.	in the presence of alkali metal	temp., °C	duration of electrolysis, min	yield,%	
La	3.98	7	Li	30	60	99.5	43
Ce	3.98	7	Li	30	60	93.0	43
Nd	3.98	7	Li	30	60	79.2	43
Pm	3.98	7	Li	30	60	84.3	43
Pm	3.98	7	K	30	60	12.7	43
Pm[a]	100	6	K	0—2	90	83.5	47
Pm[b]	100	6	Li	0—2	60	96.7	47
Er	3.98	7	Li	30	60	18.5	43
Lu	3.98	7	Li	30	60	8.8	43

[a] Trace amounts. [b] In the presence of samarium (8.8 mg ml^{-1}).

Table 3. Effect of alkali metal amalgams on the isolation of certain rare-earth elements[42].

Amalgam	Yield, %								
	^{140}La	^{144}Ce	^{147}Nd	^{147}Pm	^{152,154}Eu	^{91}Y	^{169}Er	^{175}Yb	^{177}Lu
Lithium	99.5	93.0	89.2	84.3	99.0	90.5	18.5	86.7	8.8
Potassium	—	18.0	37.0	12.7	98.7	19.8	11.0	76.1	7.5
Caesium	70.0	14.6	35.0	8.0	96.0	7.8	8.5	53.6	6.2

The type of alkali metal amalgam has the main effect on the yield of the rare earth (Table 3). Tables 2 and 3 show that lithium amalgam favours the most complete separation of the rare earth; cerium group elements are more readily isolated than the elements of the yttrium group (see also Fig. 2). The smallest yield is obtained with erbium and lutetium. The effect of the excess of complex-forming ligand and of the concentration of rare earths which do not have a stable divalent state on the degree of their separation is smaller than in the isolation of europium, ytterbium, and samarium. Differences of this kind are used for the enrichment and separation of rare earths,

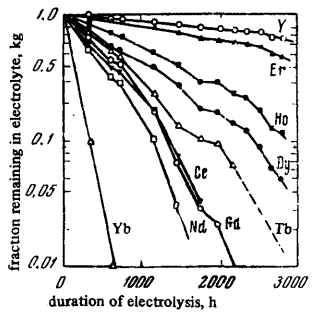

Figure 2. Dependence of the degree of liberation of certain rare-earth elements at a mercury cathode on the duration of electrolysis[46,88].

which can be divided into three groups as regards the relative ease of their electrolytic deposition at a stationary mercury cathode: (1) elements of the cerium group; (2) elements with a stable divalent state under the electrolysis conditions (europium, ytterbium, and samarium); and (3) elements of the yttrium group.

III. MECHANISM OF THE REDUCTION OF RARE-EARTH ELEMENTS

The mechanism of the reduction of rare earths at a mercury cathode was investigated mainly in two ways—in connection with the extraction of rare-earth elements by alkali metal amalgams and polarographically. In the first studies on the conditions of isolation of ytterbium at a mercury cathode[34,35] it was already shown that ytterbium is initially reduced to the divalent state and then to the metal, forming an amalgam with mercury. Somewhat later a similar mechanism was proposed also for the reduction of europium and samarium[38,41,47]. The two-stage reduction of europium, samarium, and ytterbium and also of certain other rare-earth elements is demonstrated by numerous facts, mainly by the presence of two waves in polarograms obtained at a dropping mercury cathode[54-62], corresponding to the consecutive reduction of triply-charged ions to doubly-charged species and then to the metal with formation of an amalgam.

More complex relations indicating a different cathodic process were obtained in other investigations[63-74].

It has been shown[41,47,50] that the transfer of samarium, cerium, and promethium to the mercury cathode is due to electrolytic reduction. However, in the electrolysis of acetate–citrate solutions more complex chemical reactions take place than was believed earlier[35]. The anions Ac^-, H_2Cit^-, $HCit^{2-}$, and Cit^{3-} form ionic complexes of different compositions with rare-earth cations. Their relative concentrations depend on the pH of the solution, the instability constant, and the ratio of the concentrations of the rare earths and the complex-forming ligands. The optimum conditions for electrolysis are thus directly related to the correct choice of ligand[32,33,43]. Apart from the rare earths, the alkali metal and hydrogen cations are reduced at the mercury cathode; the order of their reduction depends on the relative potentials and the pH of the solution. In the presence of complex-forming ligands the reduction potentials of the rare earths, which can be

estimated from the half-wave potentials (Table 4), are displaced towards more negative values and approach under the experimental conditions the reduction potential of alkali metal (Table 5). Consequently the efficiency of the deposition of rare-earth elements is related to the difference between the potentials of the alkali metal and the element being deposited. Thus in the presence of lithium, which has a more negative reduction potential than potassium, caesium, and sodium, the rate and degree of isolation of rare-earth elements are higher.

Table 4. Half-wave potentials of rare-earth elements[54].

Reaction	$E_{1/2}$, V	Composition of electrolyte
$La^{+3} \rightarrow La^0$	−1.92	in the presence of 0.01 M LiCl
$Ce^{3+} \rightarrow Ce^0$	−1.97	ditto
$Pr^{3+} \rightarrow Pr^0$	−1.75	in the presence of 0.1 M LiCl, 0.01% gelatine, and 2.5×10^{-3} M Pr^{3+}
$Pr^{3+} \rightarrow Pr^0$	−1.82	in the presence of 0.1 M LiCl, 0.01% gelatine, and 8.9×10^{-3} M Pr^{3+}
$Nd^{3+} \rightarrow Nd^0$	−1.81	in the presence of 0.1 M LiCl, 0.01% gelatine, and 4.1×10^{-3} M Nd^{3+}
$Nd^{3+} \rightarrow Nd^0$	−1.77	in the presence of 0.1 M LiCl, 0.01% gelatine, and 1.6×10^{-3} M Nd^{3+}
$Sm^{3+} \rightarrow Sm^{3+}$	−1.77	in the presence of 0.01 M LiCl, 0.01% gelatine, and 5.0×10^{-3} M Sm^{3+}
$Sm^{3+} \rightarrow Sm^0$	−1.96	ditto
$Eu^{3+} \rightarrow Eu^{2+}$	−0.78	in the presence of 0.01 M LiCl.
$Eu^{3+} \rightarrow Eu^0$	−2.14	ditto
$Gd^{3+} \rightarrow Gd^0$	−1.74	in the presence of 0.1 M LiCl and 8×10^{-4}M Gd^{3+}
$Tb^{3+} \rightarrow Tb^0$	−1.85	in the presence of 0.1 M LiCl and 0.005% gelatine
$Dy^{3+} \rightarrow Dy^0$	−1.85	–
$Ho^{3+} \rightarrow Ho^0$	−1.85	–
$Er^{3+} \rightarrow Er^0$	−1.85	–
$Tu^{3+} \rightarrow Tu^0$	−1.85	–
$Yb^{3+} \rightarrow Yb^{2+}$	−1.17	in the presence of 0.1 M LiCl, 0.005% gelatine,
$Yb^{3+} \rightarrow Yb^0$	−2.05	and 5×10^{-4}M Yb^{3+}
$Lu^{3+} \rightarrow Lu^0$	−1.8	–

Table 5. Standard potentials and half-wave potentials of alkali metals at the mercury electrode (relative to the saturated calomel electrode[75].

Metal	E^0, V	$E_{1/2}$, V	$E_{1/2}-E^0$, V
Li	−3.25	−2.26	+0.99
K	−3.16	−2.12	+1.04
Na	−2.99	−2.04	+0.95

Shvedov and Fu I-pei[42,43] give preference to amalgam cathodes. However, it is noteworthy that the deposition of rare-earth elements at a mercury cathode cannot be explained by simple replacement of alkali metal ions in the amalgam; this is confirmed by the data of Shvedov and Fu I-pei[41] concerning the constancy of the concentration of caesium in the solution during the electrolysis of europium. It is most likely that the efficiency of the isolation of rare-earth elements at an amalgam cathode is related, as mentioned above, to the difference between the potentials of the alkali metal and the element being isolated and that the alkali metal in the amalgam behaves as an additional reducing agent.

A large number of rare-earth amalgams obtained in electrolysis with a mercury cathode and by the extraction method have been investigated polarographically and electrochemically. For example, Barrett carried out the extraction of rare-earth elements with about 0.1% alkali metal amalgams from acetate media at pH 4 until the onset of precipitation of the hydroxide[63,64]. Lanthanum, cerium, praseodymium, and neodymium and also samarium, europium, and ytterbium were extracted. The results are presented in Table 6, which shows that the degree of extraction of the elements of the lanthanum–neodymium group decreases in the sequence lithium > sodium > > potassium, while the sequence for europium, samarium, and ytterbium is different: sodium > potassium > lithium, the degree of extraction also decreasing with decrease of the concentration of the alkali metal (Fig. 3). The measured potentials of most of the rare-earth amalgams prove to be lower than those of the corresponding alkali metal amalgams. This evidently accounts for Barrett's[63,64] observation of only single reduction waves at potentials in the range 1.84–2.04 V.

Table 6. Percentage extraction of rare-earth elements by potassium, sodium, and lithium amalgams[63] (c_{Ln} = 0.5 M).

Rare earth	Amalgam*		
	Li	Na	K
La	38	21	17
Ce	—	13	8
Pr	31	13	14
Nd	23	7	5
Sm	45	66	50
Eu	41	50	50
Yb	25	47	37

* 0.04 M amalgam was used.

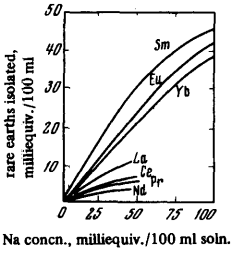

Figure 3. Variation of the degree of extraction of rare-earth elements with the concentration of sodium amalgam[56].

Samarium, europium, and ytterbium are extracted to a higher extent than elements of the lanthanum–neodymium group; the degree of extraction falls with increasing atomic number of the element and does not correspond to the stability of divalent ions in solution. This may be because rare-earth elements form with acetate ions complexes of indefinite composition and low stability, which is independent of the atomic number of the element[76], and also may be associated with hydrolytic phenomena. The size of hydrated rare-earth cations is known to increase with their atomic number[77], which accounts for the increasing tendency of rare earths towards hydrolysis on going from lanthanum to lutetium[78–80]. Biedermann and Giavatta[81] showed that in solution at pH ≥ 6.5 lanthanum is hydrolysed, forming ions of the type $La(OH)^{2+}$ and $La_2(OH)^{5+}$. In this connection, it is logical to expect the formation of

hydrolysed rare-earth species at a lower pH when the atomic number is higher. Thus hydrolysis, which includes also the formation of non-reducible polynuclear ions, can explain the observed tendency of the extraction coefficient to decrease with increasing atomic number. This can also account for the behaviour of non-extractable rare-earth elements:

$$Ln^{3+} + nH_2O + Na \rightleftarrows Ln(OH)^{2+} + Na^+ + H \cdot$$

However, there is no direct proof of the formation of intermediate rare-earth ions in the extraction of elements of the lanthanum–neodymium group[82,83].

The data of Barrett et al.[64] supplement the classification of these elements given above. In extraction by alkali metal amalgams elements of the first group (lanthanum–neodymium) are reduced in one stage[64]. Since the extraction process is the sum of the electrochemical and hydrolytic processes and the tendency towards hydrolysis increases with the atomic number, three-electron reduction becomes impossible for samarium, europium, and ytterbium (second group), which are reduced in two stages. The third group (gadolinium–lutetium) does not have a divalent state and three-electron reduction can be achieved only under very severe conditions in view of the increasing tendency of these elements towards hydrolysis, and for this reason they are hardly reduced by alkali metal amalgams.

The reduction of samarium, europium, and ytterbium takes place in stages, the divalent rare-earth cations formed initially showing some similarity to the alkaline earth elements. In this case the degree of hydrolysis is low, since, for example, europium(II) hydroxide is appreciably soluble in an alkaline solution. Furthermore, divalent rare-earth cations are hydrolysed at higher pH, in contrast to the trivalent cations, which is important in their subsequent reduction to the metal under conditions of a higher hydroxide ion concentration near the cathode than in the bulk phase. This in fact explains why unhydrolysed rare-earth cations are capable of stepwise reduction by alkali metal amalgams in the opposite sequence, i.e. sodium > potassium > lithium.

Treindl[84] made a polarographic and oscillographic study of certain rare earths. On the basis of data showing the high reducing power of the reduction products obtained, the presence of hydroxide ions at the overvoltage potential[85], the dependence of the depth of the minima on the capacity of the anions for deformation and on their concentration, the dependence of the limiting current on the concentration of deformable anions, etc., he suggested that the reduction products are the hydrides and halide hydrides of the corresponding rare earths:

$$xH^+ + 2xe^- = xH^-,$$
$$Ln^{3+} + xH^- + (3-x)X = LnH_xX_{3-x},$$
$$LnH_xX_{3-x} + xH_2O = Ln^{3+} + (3-x)X + xH_2 + xOH^-,$$
$$H^+ + 2e^- + H_2O = H_2 + OH^-,$$

where $x = 1, 2, 3$ and X is a halide ion. The quantitative proportions of the hydrides depend on the electrode potential.

It was established[86,87] that in the presence of 0.1 M lithium chloride at pH 4 all rare-earth elements give rise to a double reduction wave and are reduced irreversibly at a dropping mercury cathode; the diffusion-limited waves observed in some studies[65–74] can be caused by the reduction of hydrogen in the aquo-complexes of these elements:

$$Ln(H_2O)_6^{3+} \rightarrow Ln(H_2O)_{6-x}(OH)_x^{3-x} + xH,$$
$$xH^+ + xe^- \rightarrow x/2\,H_2,$$
$$Ln(H_2O)_6^{3+} + xe^- = Ln(H_2O)_{6-x}(OH)_3 + x/2\,H_2.$$

On the basis of data derived from the electrochemical separation of rare-earth elements at a mercury cathode in the presence of lithium ions and various complex-forming ligands (acetate, perchlorate, tartrate, and citrate ions), Onstott[88] explained the reduction of rare-earth elements (without a stable divalent state) by the formation of hydrides according to the following mechanism:

$$[Ln(H_2O)A_m]^{3+} + e^- \xrightarrow{\text{fast}} [Ln(H)(OH)A_m]^{2+}$$
$$\downarrow e^- \ (\text{slow})$$
$$[Ln(H)(OH)A_m]^+$$
$$[Ln(H)(OH)A_m]^+ + 2e^- \rightleftarrows LnH(Hg) + OH^- + mA.$$

It is noteworthy that the electrolytic reduction of rare-earth elements at a mercury cathode is still insufficiently elucidated. The data of the investigations quoted above make it possible to distinguish the following main types of cathodic processes.

Consecutive reduction to the metal with formation of an amalgam:

$$Ln^{3+} + e^- \rightarrow Ln^{2+},$$
$$Ln^{2+} + 2e^- \rightarrow Ln^0(Hg).$$

Direct reduction of triply charged rare-earth ions to the amalgam:

$$Ln^{3+} + 3e^- \rightarrow Ln^0(Hg).$$

Reduction with formation of hydrides and halides hydrides:

$$Ln^{3+} + xH^+ + 2xe^- + (3-x)X^- = LnHxX_{(3-x)}.$$

Reduction of hydrogen in the aquo-complexes or in the hydrate shells of the rare-earth ions:

$$Ln(H_2O)x^{3+} + 3e^- \rightarrow Ln(OH)_3 + (x-3)H_2O + {}^3/_2\,H_2.$$

For rare-earth elements without a stable divalent state, the last two types, in which the cathodic process is regarded as catalytic reduction of hydrogen ions, are the most likely; the mechanism of the catalysis consists in the formation and decomposition of hydrides[87].

IV. SEPARATION OF RARE-EARTH ELEMENTS

1. Conditions of Electrochemical Separation

The separation of rare-earth elements by electrolysis with a mercury cathode depends on the relative distribution of the rare-earths between mercury and the electrolyte. In other words, any parameter which influences the properties of the rare-earth elements in each phase will influence their relative distribution between the two phases[70]. For example, the formation of rare-earth complexes in the aqueous phase complicates the electrolysis. The degree of complication is greater the more stable are the complexes.

The equilibrium distribution of any trivalent element between the mercury phase and the electrolyte at 25°C can be formulated[46]‡ as follows in accordance with the Nernst equation:

$$E = E^a - 0.02\log(c^a/c^e), \quad (1)$$

where E is the cathode potential, E^a the standard potential of the amalgam, c^a the concentration of the rare earth in the amalgam, and c^e its concentration in the electrolyte.

‡ In the calculations account was not taken of the irreversibility of the cathodic-anodic behaviour of rare-earth elements. Nevertheless, they can be used for practical purposes.

The cathode potential E is the same for the electrode processes of any two rare earths (1 and 2) and therefore the distribution is described by the equation:

$$\Delta E = E_1^a - E_2^a = 0.02 \log (c_1^a \, c_2^e / c_1^e \, c_2^a) . \quad (2)$$

Eqn. (2) shows that the partition coefficient is a constant quantity, which depends only on the difference between the amalgam potentials (ΔE) of any two rare-earth elements. For example, a difference as low as $\Delta E = 20$ mV corresponds to a partition coefficient of 10.

To describe the separation of a mixture of trivalent rare-earth elements, data on standard electrode potentials can also be invoked, particularly if the amalgam potentials have been determined imprecisely. The amalgam potentials of rare-earth elements differ approximately to the same extent as their standard electrode potentials and therefore differences between the potentials of adjacent rare-earths of approximately 20 mV permit satisfactory separation, as stated.

For practical separation of two adjacent rare-earth elements, account must be taken of the purity and the yield of each element. For this purpose, it is necessary to determine the cathode potential from the known values of E_1^a or E_2^a, which can be done with the aid of Eqn. (2). It is also possible to predict whether or not the separation of divalent from trivalent rare-earths is possible. For the description of the reduction of divalent rare-earth elements, Eqn. (1) becomes

$$E_{II} = E_{II}^a - 0.03 \log (c_{II}^a / c_{II}^e) . \quad (3)$$

From Eqns. (1) and (3), we obtain

$$3E - 2E = 3[E^a - 0.02 \log (c^a/c^e)] - 2[E_{II}^a - 0.03 \log (c_{II}^a / c_{II}^e)]$$

and therefore

$$E = 3E^a - 2E_{II}^a - 0.06 \log \alpha , \quad (4)$$

where α is the separation factor, which depends on the cathode potential.

If equilibrium distribution is attained simultaneously for both electrode processes, the variation of E should be represented by a straight line. The time of attainment of a stable cathode potential after optimum equilibrium is reached is determined by the values of E^a and E_{II}^a. In the presence of a complex-forming ligand, Eqn. (2) becomes, from the law of mass action,

$$E_1^a - E_2^a = 0.02 \log \alpha + 0.02 \log \frac{K_{d_2}}{K_{d_1}} , \quad (5)$$

where K_d is the instability constant. If the ligand is a very powerful complex-forming agent, for example EDTA, separation may be difficult because of the high potential necessary to break down the complex.

Complex formation can alter the conditions of the deposition of rare-earth elements and can have a favourable effect on their separation when the complex-forming agent is chosen correctly [33,43].

As already stated, direct deposition of rare-earth elements at a mercury cathode depends on the distribution of their ions between mercury and the electrolyte [46,89] and on the rate of transfer of rare-earth ions through the electrode–electrolyte interface, which is defined by the following equation:

$$-\frac{dc}{dt} = \frac{DA}{V\delta}(c - c^e), \quad (6)$$

where c is the concentration of the diffusing ion in the electrolyte, c^e the concentration of the ion on the surface of the electrode, t the duration of electrolysis, D the diffusion coefficient, A the area of the electrode, V the volume of the electrolyte, and δ the thickness of the diffusion layer.

Integration of Eqns. (6) with $c^e = 0$ yields

$$\ln \frac{c}{c^0} = -\frac{DA}{V\delta} t , \quad (7)$$

where c^0 is the initial concentration of the ions in solution. The plot of $\ln c$ against t is a straight line with slope $DA/V\delta$, which can be regarded as a rate constant (k).

Rare-earth elements present in the electrolyte at low concentrations are hydrolysed at a rate which is mainly determined by diffusion in the region near the electrode [90–92]. The rate of diffusion depends in turn on the concentration at the mercury surface of the ions undergoing electrolysis. When $k = DA/V\delta$, Eqn. (7) is of the form

$$dN/dt = k \, c^s , \quad (8)$$

where N is the number of ions per unit area transferred during time t from the surface of the electrode on which the concentration of ions is c^s. [93] The rate of removal of c^s is determined by the quantity $D(dc/dl)$, where D is the bulk-phase diffusion coefficient of the ions and l the distance from the electrode. In a stirred solution the bulk-phase concentration c^b does not vary significantly with δ, so that

$$dN/dt = D(c^b - c^s)/\delta = k \, c^s . \quad (9)$$

Since c^b depends on time, we obtain

$$-\frac{dc^b}{dt} = \frac{dN}{dt} \times \frac{A}{V} = \frac{\frac{A}{V} \times D k \, c^b}{D + \delta k} . \quad (10)$$

At the extreme values of the parameters δ, D, and k, for example when $\delta k \gg D$, Eqn. (10) acquires the form of Eqn. (6), which reflects Fick's first law applied to electrode reactions [57]. When $\delta k \ll D$, we obtain $-dc^b/dt = (A/V)kc^b$. In this case $c^s \simeq c^b$ and the rate is almost independent of D and δ.

Eqn. (10)can be used to describe the rare-earth separation processes, and one can write

$$-\frac{dc^b}{dt} = \frac{A}{V} \beta \, c^b \quad (11)$$

where $\beta = Dk/(D + \delta k)$.

The ratio of the concentrations of the two rare earths in the electrolyte after a time t can be represented by the relation

$$\frac{c_2^b}{c_1^b} = \frac{c_2^0}{c_1^0} e^{\frac{A}{V}(\beta_1 - \beta_2)t} , \quad (12)$$

where c_1^0 and c_2^0 are the initial concentrations of the rare earths. This ratio is high for high values of t when $\beta_1 \gg \beta_2$.

Since the concentration of any of the two rare earths in the amalgam is defined as $c_i^a = (c_i^0 - c_i^b)V_e/V_a$, where V_e/V_a is the ratio of the volumes of the electrolyte and the amalgam, the ratio of the rare earths transferred to the amalgam is given by the equation

$$\frac{c_1^a}{c_2^a} = \frac{c_1^0 \left(1 - e^{-\frac{A}{V}\beta_1 t}\right)}{c_2^0 \left(1 - e^{-\frac{A}{V}\beta_2 t}\right)} . \quad (13)$$

For low values of t, the ratio $c_1^a/c_2^a \simeq (c_1^0/c_2^0)(\beta_1/\beta_2)$; for high values of t, when the electrolysis of both rare earths is almost complete, $c_1^a/c_2^a \simeq c_1^0 c_2^0$.

Knowing the rate of deposition of any two rare-earth elements at the mercury cathode and their partition coefficients between the two phases, it is possible to predict the efficiency of the separation of the rare earths. The partition coefficient of two rare-earths (1 and 2) deposited simultaneously at a mercury cathode depends on the ratio of their concentrations in the electrolyte (c^e) and in the amalgam (c^a), i.e.[88]

$$\alpha = \frac{c_1^a c_2^e}{c_2^a c_1^e} \quad . \qquad (14)$$

When c_1^a, c_2^a, c_1^e, and c_2^e from Eqns. (12) and (13) are substituted in Eqn. (14), we obtain

$$\alpha = \frac{[1 - e^{-\frac{A}{V}\beta_1 t}]}{[1 - e^{-\frac{A}{V}\beta_2 t}]} \times e^{\frac{A}{V}(\beta_1 - \beta_2)t} \quad . \qquad (15)$$

It follows from Eqn. (15) that, when $\beta_1 = \beta_2$, we have $\alpha = 1$ and there is no separation. For low values of t, $\alpha \simeq \beta_1/\beta_2$; when $t \to \infty$, we have

$$\log \alpha = \frac{At}{V \times 2.303}(\beta_1 - \beta_2) \quad . \qquad (16)$$

Eqn. (16) shows that, when the transfer of both rare earths to mercury is almost quantitative, the ratio of the concentrations of the rare earths remaining in the electrolyte becomes very high. In this case α may be very large compared with the value obtained under conditions of equilibrium separation where α is constant. Fig. 4 shows a plot of α (calculated with the values of β_1/β_2 adopted) for the transfer of rare earth 1 (Ln).

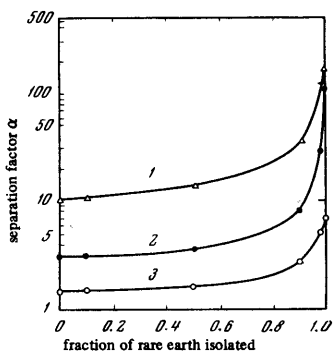

Figure 4. Variation of the separation factor α with the ratio β_1/β_2:[88] *1*) $\beta_1/\beta_2 = 10$; *2*) $\beta_1/\beta_2 = 3$; *3*) $\beta_1/\beta_2 = 1.5$.

In the separation of samarium and europium[8] the results obtained do not meet the requirements of equilibrium separation, but they can be used to obtain a general idea about the rate of the forward reaction. Thus it has been established that 90% of europium is extracted during 55 min of electrolysis of 20.4% of samarium after 230 min; then the ratio $\beta_1/\beta_2 = 42$. It follows from Eqn. (15) that, for 99 and 99.9% of extraction of europium, $\alpha = 856$ and 5570 respectively. These values agree fairly well with the measured α, which is respectively 974 for 99.2% extraction and 2810 for 99.9% extraction of europium[88].

More complete data were obtained in experiments on the separation of europium and samarium where the cathode potential was high and the extraction of europium was almost quantitative[46]; these are presented in Table 7, which shows that α increases rapidly when the degree of extraction of europium is high.

Table 7. Electrolysis of the citrate complexes of europium and samarium at a lithium amalgam cathode in alkaline solutions (cathode potential 2.3–3.0 V, t = 30–39°C)[88].

Extraction, %		α
Eu	Sm	
99.73	18.7	1600
99.83	17.6	2700
99.84	14.6	3700
99.95	26.2	5600
99.96	15.9	13 200

The rate equation for the reaction can be used also to determine the time required for the isolation of the rare earth (europium) at the required concentration[46]. It is noteworthy that better agreement between experimental and calculated data is observed for dilute solutions (Fig. 5, curve *2*).

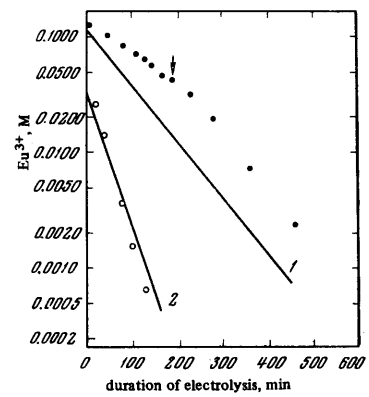

Figure 5. Electrolysis of europium solutions[46]: *1*) volume of electrolyte 498 ml, $c_{Eu^{3+}} = 0.12$ M, $c_{Sm^{3+}} = 0.37$ M; *2*) volume of electrolyte 285 ml, $c_{Eu^{3+}} = 0.039$ M, $c_{Sm^{3+}} = 0.32$ M (current density ~ 14 mA cm^{-2}; amount of mercury 150 ml). Circles—experimental data; straight lines—calculated data; the arrow indicates the renewal of mercury.

It is also possible to calculate α and β for rare earths without a stable divalent state. On the basis of experimental data for the electrolysis of trivalent rare-earth elements presented in Fig. 2, Onstott[88] obtained a series of values of the ratio β_1/β_2 (Table 8). Comparison with the observed and calculated values for a mixture of rare earths at a different concentration shows that β_1/β_2 is

almost the same and independent of the rare-earth concentration ratios in the mixture. The observed variation of β_1/β_2 with the separation factor α is shown in Fig. 4.

2. Examples of the Separation of Certain Rare-Earth Elements

On the basis of the conditions which they developed for the isolation of europium, ytterbium, and samarium, Ryabchikov and coworkers[35,40,44] described the possible ways of separating these elements. Europium can be separated from ytterbium by the electrolysis of their acetate–citrate solutions at high pH and it can be separated from samarium at an $Ln^{3+}:Cit^{3-}$ ratio $> 1:2$. Conditions have also been found for the isolation of ytterbium from a mixture of the elements of the yttrium group[94,95].

Table 8. The ratios β_1/β_2 for a methanol electrolyte containing rare-earth elements.

Rare earth	β_1/β_2 1 (initial mixture)	β_1/β_2 2 (enriched mixture)	Rare earth	β_1/β_2 1 (initial mixture)	β_1/β_2 2 (enriched mixture)
Nd—Gd	1.4	1.9	Dy—Ho	1.5	2.0
Gd—Tb	1.3	1.3	Ho—Er	2.5	2.0
Tb—Dy	1.3	1.5	Er—Y	1.6	1.2

Onstott[37] showed that lithium amalgam is best for the isolation of europium; when potassium citrate is replaced by lithium citrate, the yield of samarium changes only slightly[39]. Onstott notes that samarium, europium, and ytterbium can be separated from other rare earths (whose deposition at a mercury cathode requires more severe conditions) and also from one another if they are present at different concentrations. For example, for an initial ratio of europium and samarium of 1:62 (0.447 M samarium and 7.2×10^{-3} M europium), the concentration of the europium impurity in samarium can be reduced by a thousand-fold by electrolysis.

Shvedov and Antonov[52] investigated the conditions of the separation of samarium from neodymium and praseodymium at different concentrations of the elements (ranging from 0.1 to 1.34 M) in the presence of lithium tartrate at a current density of 15.5 mA cm^{-2}. The proportions of samarium, neodymium, and praseodymium were equimolar, i.e. 1:1:1. It was established that an increase of the concentration of lithium tartrate does not influence the liberation of samarium, and neodymium and praseodymium at tartrate concentrations of 0.4 and 0.7 M respectively do not form amalgams and are not liberated at the mercury cathode. Neodymium and praseodymium can be separated[52] at a current density of 7.7 mA cm^{-2} and a tartrate concentration of 0.34 M. Thus during 60 min electrolysis 47% of praseodymium and 1.5% of neodymium were liberated from 20 ml of solution at a 200 g mercury cathode; the separation factor was 58.

Clusius and Ramirez[96] used the slight differences in the mobilities of neodymium and praseodymium ions for the separation of the elements. Onstott[97] studied the possibility of the separation of the elements by the electrolysis of their chlorides in the presence of lithium citrate. The maximum separation factor in this process was 3.

Lavrukhina and coworkers made a detailed study of the conditions governing the liberation of samarium at a mercury cathode[47–50] and, using the differences in the behaviour of promethium, cerium, and other rare-earth elements, they proposed a method for their separation. In particular, on periodic addition of potassium citrate during electrolysis (the ratio $Ln^{3+}:Cit^{3-}$ decreases) or on renewal of mercury (the electrode potential remains constant and insufficient for the liberation of promethium and cerium), rare-earth elements without a stable divalent state remain in solution. This method was used for the separation of the products of nuclear reactions, the radioisotopes of lanthanum, cerium, praseodymium, neodymium, and promethium, from the main bulk of samarium and europium irradiated by protons having energies between 220 and 660 MeV.[48,49,98,99,100] Radioactive isotopes of the yttrium group elements were separated by the electrolysis of their acetate–citrate solutions from ytterbium irradiated with high-energy protons[101].

Shvedov and Antonov suggested a scheme for the separation of yttrium, ytterbium, and erbium, and lutetium, and also europium and lanthanum[42,43]. They investigated[53] the conditions for the formation of gadolinium, terbium, dysprosium, and holmium amalgams in the electrolysis with a mercury cathode of the acetate–citrate solutions in the presence of lithium ions. It was established that the concentration of lithium ions, the molar ratio $Ln^{3+}:Cit^{3-}$, and the concentration of the rare earths have a considerable influence on the yields of the elements. The optimum molar ratios $Ln^{3+}:Cit^{3-}$ are different for gadolinium, terbium, holmium, and dysprosium, amounting respectively to 12–15, 13, 26, and 17. The following separation factors have been found for binary mixtures of rare-earth elements[53]: 6–8 for gadolinium–terbium, 10–40 for gadolinium–holmium, 5–10 for terbium–dysprosium, 10–30 for terbium–holmium, 20–40 for terbium–erbium, and 30–60 for terbium–thulium. The yield of the rare-earth elements as a rule decreases with their concentration. For example, at a concentration in excess of 0.01 M holmium is not liberated at a mercury cathode; the transfer of dysprosium and terbium to the amalgam becomes negligible when their concentrations in the electrolytes are greater than 2.5×10^{-2} M and 4.0×10^{-2} M. This is associated with the smaller degree of dissociation of the complexes of these rare-earth elements as their concentration is raised.

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In the development of a number of new manufacturing processes and the current extensive application of semiconductor materials the problem of the preparation of ultrapure substances and the determination of many elements as impurities at very low concentrations (down to 10^{-10}%) has become particularly urgent[102,103]. In this respect electrolysis with a mercury cathode is one of the promising methods for the concentration of elements with their subsequent determination by different procedures.

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Some Electrochemical Properties of Mercury

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The first information about the application of mercury as an electrode material dates back to the end of the 19th century[1]. At the same time it was noted that mercury is not an indifferent metal and is capable of reacting with a number of ions in solution. Further extensive application of mercury as an electrode material stimulated systematic investigation of its electrochemical properties: electrocapillary phenomena at the mercury–solution interface, equilibrium and steady-state potentials, kinetics and mechanism of the discharge-ionisation process at the equilibrium and steady-state potentials, and reducing and other properties of mercury. These questions are discussed in the present review. The bibliography comprises 65 references.

CONTENTS

I. Electrocapillary phenomena at the mercury-solution interface 710
II. Equilibrium potentials of mercury 711
III. Kinetics and mechanism of the electrochemical oxidation of mercury 712
IV. Reducing properties of mercury 714

I. ELECTROCAPILLARY PHENOMENA AT THE MERCURY–SOLUTION INTERFACE

The electrical double layer arising under equilibrium conditions at the mercury–solution interface is known to consist of anions in the liquid component, the surface of the mercury being positively charged relative to the liquid. The displacement of the potential towards negative values leads to a decrease of the concentration of anions in the double layer. On further displacement of the potential, the charge of the double layer is reversed. The change in potential and the associated charge reversal of the double layer alters the surface tension of mercury.

The first measurement of the surface tension of mercury as a function of the applied potential was made by Lippman[2] with the aid of the capillary electrometer of his design. Paschen[3] and then Gouy[4,5] made systematic studies on the surface tension of mercury as a function of the potential in solutions of different electrolytes (hydrochloric acid, sulphuric acid, nitric acid, potassium hydroxide, etc.) and determined the form of the capillary curve. In all cases the dependence of the surface tension of mercury on the applied potential was represented by a curve passing through a maximum. The maximum surface tension corresponds to the zero charge of the mercury surface. The surface tension and correspondingly the surface energy of the electrode are a maximum at this point.

Adsorption of anions displaces the electrocapillary maximum towards more negative potentials, while adsorption of cations has the opposite effect. Anions can be arranged in the same depolarising effect sequence as that of their effect on the surface tension of mercury. Thus, in the series of anions $NO_3^- < SO_4^{2-} < Cl^- < Br^- < < CN^- < S^{2-}$ their depolarising effect increases from NO_3^- to S^{2-} and the shift of the electrocapillary maximum of mercury towards negative potentials increases in the same direction.

The nature of the anion influences not only the equilibrium or steady-state potential of mercury but also the essential features of the potential-determining process. Members of the Soviet electrochemical school have played

a considerable role in the study of this problem. By deepening and extending their studies in this field, Soviet electrochemists have arrived at important conclusions concerning the nature of these phenomena and their influence on the kinetics of electrode processes.

II. EQUILIBRIUM POTENTIALS OF MERCURY

One of the most important electrochemical characteristics of mercury are the potentials of the equilibrium system comprising mercury and a solution of its ions. The potential jump at the metal–solution interface is known to be established and stabilised by the mutual compensation of two opposed processes:

$$M^0 \rightleftarrows M^{n+} + ne .$$

On the other hand the potential jump can also occur as a result of the adsorption of ions and dipolar molecules. The effect of the last process is shown when the metal ions are absent from the solution. In the presence of the metal ions an equilibrium state is established, characterised by the equality of the rates of two opposed processes. The potential of such an electrode can be calculated from the familiar Nernst formula. The simultaneous occurrence of side reactions brings the electrode to a new state, which can be called the steady state.

The first reliable data on the equilibrium potential of the system $Hg-Hg_2^{2+}$ were obtained by Brodskii[6-8]. From measurements of the e.m.f.'s of the concentration cells $Hg\,|\,Hg_2(NO_3)_2,\ c_n\,|\,KNO_3,$ sat. $|\,Hg_2(NO_3)_2,\ c_1\,|\,Hg$, he determined fairly accurately the activity coefficient of Hg_2^{2+} ions. The normal potential of the system $Hg-Hg_2^{2+}$ was calculated from the formula

$$\varphi^0 = \varphi - \frac{RT}{2F}\ln f c ,$$

where c is the concentration of Hg_2^{2+} ions and f their activity coefficient. According to Brodskii's data, the potential φ^0 of this system at 19.2°C is 0.804 V (relative to the normal hydrogen electrode).

Three potential-determining processes are usually considered for the system mercury–solution:

$$Hg^{2+} + 2e \rightleftarrows Hg^0 ,$$
$$Hg_2^{2+} + 2e \rightleftarrows 2\,Hg^0 ,$$
$$2\,Hg^{2+} + 2e \rightleftarrows Hg_2^{2+} .$$

The potential of the mercury electrode in a solution of a mercurous salt is

$$\varphi_{Hg,\,Hg_2^{2+}} = \varphi^0_{Hg,\,Hg_2^{2+}} + \frac{RT}{2F}\ln a_{Hg_2^{2+}} .$$

Expressing the ionic activity $a_{Hg_2^{2+}}$ in terms of the activity product of, for example, mercurous chloride, and the activity of chloride ions, we obtain the expression

$$\varphi_{Hg,\,Hg_2Cl_2} = \varphi^0_{Hg,\,Hg_2Cl_2} - \frac{RT}{F}\ln a_{Cl^-} ,$$

where φ^0_{Hg,Hg_2Cl_2} is the normal potential of the calomel electrode (corresponding to unit activity of chloride ions).

Thus it has come to be assumed that the system $Hg-Hg_2^{2+}$ is potential-determining for the calomel electrode. However, the equilibrium in solutions of mercurous salts in the presence of certain anions (halide, cyanide, etc. ions) is more complex than is usually assumed[10]. Ogg[11] established that, when a solution of mercuric salt is shaken with metallic mercury, divalent mercury is not quantitatively converted into the monovalent form, but the following equilibrium is set up:

$$Hg_2^{2+} \rightleftarrows Hg^0 + Hg^{2+} .$$

In the presence of a large excess of chloride, the equilibrium is displaced to the right owing to the formation of the weakly dissociated complex $HgCl_4^{2-}$:

$$Hg_2Cl_2 + 2\,Cl^- \rightleftarrows HgCl_4^{2-} .$$

Richard and Archibald[12] showed that the solubility of calomel increases in direct proportion to the square of the concentration of chloride in agreement with the above equation. It follows from this that the potential of the calomel electrode must depend on the activity of mercurous and mercuric ions and is given by the equation[10]:

$$\varphi = \varphi^0_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{a^2_{Hg^{2+}}}{a_{Hg_2^{2+}}} .$$

In the presence of an excess of chloride ions, the concentrations of mercurous and mercuric ions are low and almost equal to their activities. Then

$$\varphi = \varphi^0_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{[Hg^{2+}]^2}{[Hg_2^{2+}]}$$

or

$$\varphi = \varphi^{\circ}_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{[Hg^{2+}]}{[Hg_2^{2+}]} + \frac{RT}{2F}\ln[Hg^{2+}] .$$

The concentration ratio $[Hg^{2+}]/[Hg_2^{2+}]$ is constant[11] and equal to 1/120. Consequently

$$\varphi = \varphi^0 + \frac{RT}{2F}\ln[Hg^{2+}],$$

i.e. the potential of the mercury electrode in a solution of a mercurous or mercuric salt must be determined by the equilibrium concentration of mercuric ions. Accordingly there should exist not three standard potentials but only one, arising in consequence of the following potential-determining process:

$$Hg^{2+} + 2e \rightleftarrows Hg_2^{2+} .$$

This type of equilibrium is also established in the presence of other ligands (Br^-, I^-, CN^-, SCN^-). The potentials of mercury in the presence of a number of complex-forming ions were measured by Tarayan and Ekimyan[13], Burriel-Marti et al.[14], Bagotskaya[15], and others.

In alkali solutions monovalent mercury forms an unstable hydroxide, which decomposes according to the equation

$$Hg_2(OH)_2 \rightleftarrows Hg^0 + HgO + H_2O ,$$
$$HgO + H_2O \rightleftarrows Hg(OH)_2 .$$

Therefore in alkaline solutions in the presence of mercurous ions the mercury electrode behaves as a metal | metal oxide electrode and its potential must be a function of the pH of the solution:

$$\varphi = \varphi^0 + \frac{0.058}{2}\lg K_1[H^+]^2 ,$$

where $K_1 = SP[Hg(OH)_2]/K_w^2$ and SP is the solubility product: $SP[Hg(OH)_2] = 1.4 \times 10^{-26}$ (see Bagotskaya[15]). Therefore

$$\varphi = \varphi_0^1 - 0.058\,pH .$$

Using the above relation, it is possible to calculate φ at different pH. The measurements have been made[10,16] with the aid of a glass electrode. As the pH increases,

the potential is displaced towards more negative values (see Table).

The variation of the potential of the $Hg-Hg^{2+}$ system with the pH is plotted in Fig. 1.[17] In the region of pH 7 in the presence of complex-forming anions (Cl^-, Br^-, I^-, SCN^-), the potential is almost independent of the pH, because these are the anions of strong acids. However, in the presence of the anion of a weak acid (CN^-), the concentration of which decreases as the pH is reduced, the potential of mercury shifts towards more positive values in the acid region, with a corresponding decrease of the reducing activity of mercury.

Variation of the mercury electrode potential* with the pH in 0.01 M mercurous nitrate solution at 20°C.

pH	Potential, V		pH	Potential, V	
	calc.	expt.		calc.	expt.
1.93	0.75	0.75	4.23	0.67	0.68
2.40	0.75	0.75	5.27	0.60	0.63
3.25	0.72	0.70	6.80	0.51	0.58

* Saturated calomel electrode.

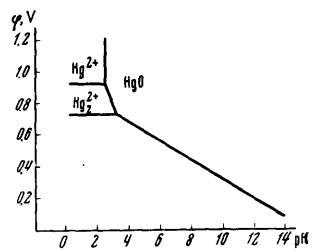


Figure 1. Effect of acidity on the oxidation-reduction potential of mercury.

Thus the equilibrium and steady-state potentials of mercury and hence its reducing properties depend to a high degree on the nature of the anion present in the solution. The effect of the anion is due to its capacity for adsorption, which is closely related to the phenomenon of complex-formation and the formation of sparingly soluble salts. The anion can influence significantly the mechanism of the oxidation of mercury. In particular, when the solution contains readily adsorbable anions (Cl^-, Br^-, I^-, etc.), the process takes place at a higher local concentration of the anions and is described by the equation

$$Hg^0 - 2e \rightleftarrows Hg^{2+}.$$

Data confirming this mechanism were obtained with the aid of non-steady-state techniques (anodic oxidation of mercury in the presence of applied constant and alternating potentials).

It has been noted[18-20] that ions adsorbed directly on the surface of mercury form mercury halides. On the other hand, in the presence of weakly adsorbed anions (NO_3^-, SO_4^{2-}) the process may be different, namely

$$2Hg^0 - 2e \rightleftarrows Hg_2^{2+}.$$

III. KINETICS AND MECHANISM OF THE ELECTROCHEMICAL OXIDATION OF MERCURY

1. Mechanism of the Anodic Oxidation of Mercury

The anodic oxidation of mercury has still been relatively little investigated. Among studies dealing with this problem, those of Ives and coworkers[21-28] and Bewick et al.[29] should first be mentioned.

The anodic oxidation of mercury has been investigated in the following ways[21-23]: (a) by studying the dependence of the potential of the mercury electrode on the amount of electricity passed through the system; (b) by recording $\varphi - t$ curves after switching off the current; (c) by recording micropolarisation curves in the intervals between current pulses in order to establish the degree of reversibility of the process; (d) by recording oscillographic $E-t$ curves with simultaneous application of alternating and constant potentials.

The anodic oxidation of mercury has been carried out[21-23] in acid (hydrochloric acid) and in neutral solutions (potassium chloride, potassium bromide, and potassium iodide) freed from atmospheric oxygen. In the study of acid solutions the polarising current density was 0.25 mA cm^{-2}. The current was interrupted after 5000 μC of electricity had been passed through. After a certain time interval the passage of current was restarted. Following the interruption of current, the variation of the potential with time was observed. Micropolarisation experiments consisted in the measurement of $I-\varphi$ curves at increasing and decreasing current densities.

The degree of reversibility was determined from the hysteresis between the ascending and descending branches of the polarisation curve or from the average slope dI/dt, which should approach infinity for ideally reversible processes.

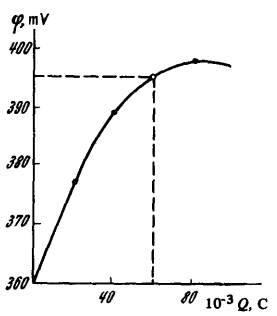


Figure 2. Variation of the mercury potential with the amount of electricity passed through the system.

The study of the dependence of the mercury electrode potential on the total amount of electricity passed through the system is of primary interest. The experimental relation[21-23] (in 0.1 N hydrochloric acid) is represented by the curve shown in Fig. 2. The measurements have shown that 6×10^{-2} C of electricity is required for the attainment of the potential of the calomel electrode (396.8 mV, 0.1 N HCl). However, if calomel were the only anodic reaction, then an incomparably smaller amount of

electricity (about 10^{-12} C) would be sufficient to saturate the entire solution (100 ml) with calomel.

Fig. 2 shows that the variation of the mercury potential with the amount of electricity passed is represented by a curve with a maximum. The potential of the maximum is more positive by 2.2 mV than that of the calomel electrode in 0.1 *N* hydrochloric acid. It has been shown[21-23] that, after the attainment of the maximum, calomel crystals are precipitated. The formation of calomel crystals is accompanied by a decrease of the potential to the value corresponding to the reversible calomel electrode. This led the authors of the above investigations to conclude that the primary product of the anodic reaction is not monovalent but divalent mercury.

The micropolarisation tests and the time variation of the mercury potential after the interruption of current confirm this view[21-23]. The observed hysteresis in the $I-\varphi$ curves disappears after a time, which suggests that the electrode attains a state of equilibrium.

$\varphi-I$ curves have two characteristic features: in the first place the potential falls slowly after the interruption of current, which suggests a slow diffusion of the potential-determining substance from the surface of the electrode; in the second place the potential is displaced towards positive values relative to that of the calomel electrode, passes through a maximum, and then falls to the potential of the calomel electrode. The authors have explained the form of the curve by the occurrence of two consecutive processes: (a) an electrochemical process—anodic generation of Hg^{2+} and (b) a non-electrical (slow but autocatalytic) process—the formation of calomel by the reaction

$$Hg^{2+} + Hg^0 \rightleftarrows Hg_2^{2+}.$$

Thus, according to these data, the product of the anodic reaction at low current densities (0.25 mA cm^{-2}) is divalent mercury; calomel forms as a result of a secondary reaction. After the attainment of equilibrium by the electrode, the reaction takes place according to the equation

$$Hg_2^{2+} + 2e \rightleftarrows 2\,Hg^0.$$

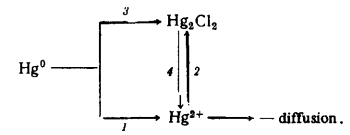
This contradicts the established view[15] concerning the nature of potential-determining processes at the equilibrium potential.

At extremely low current densities the generation of Hg_2^{2+} and Hg^{2+} ions at the equilibrium concentrations is to be expected, since the departure of the electrode from the state of equilibrium is only slight. Hg^{2+} ions arise within the double layer at a high local concentration of chloride ions, with formation of $HgCl_4^{2-}$. As a result of the formation of the complex $HgCl_4^{2-}$, prolonged cathodic polarisation following the anodic polarisation does not restore the electrode to the state of equilibrium.

Oscillographic data for this system confirm the above conclusion[21-23] concerning the mechanism of the anodic oxidation of mercury. $E-t$ curves have two peaks. The first peak is believed to correspond to the formation of Hg^{2+} ions. The rising branch of the peak comes to an end as soon as the calomel film begins to form on the surface of mercury. The horizontal section of the $E-t$ curve corresponds to the gradual coverage of the surface of mercury by the calomel film. When the coverage of the surface by calomel is complete, the discharge of chloride ions begins: the $E-t$ curve shows the corresponding rise. The chlorine liberated oxidises the calomel film, forming $HgCl^+$ ions which diffuse into the bulk of the solution. After a time the film is exhausted and the electrode returns to the non-passive state, this being accompanied by a decrease in the curve.

It has also been stated[24] that an amount of electricity greater by a factor of 10^{10} than the amount required for the saturation of the entire solution (dilute hydrochloric acid) with calomel must be passed through the mercury electrode. Under these conditions (low current density, hydrochloric acid), Hg^{2+} ions are generated. However, at a fairly high current density a small fraction of the above amount of electricity is sufficient for the attainment of equilibrium. Calomel is then generated. Such an electrode is unstable and ceases to be reversible after a short time. This spontaneous decrease of reversibility results from the disproportionation of calomel.

Thus Dibbs et al.[24] conclude that the mercury electrode can attain thermodynamic equilibrium in two different ways according to the scheme



Pathways *1* and *2* operate exclusively at low current densities, becoming superseded by pathways *3* and *4* at high current densities. An increase of the concentration of hydrochloric acid favours reactions *1* and *4*.

The problem of the kinetics and mechanism of the anodic oxidation of mercury was developed further in later investigations[25-28], where solutions containing potassium chloride, potassium bromide, and potassium iodide were studied together with hydrochloric acid. The effect of anions on the kinetics of anodic oxidation of mercury in acid and alkaline solutions has been investigated in detail[15,30,31]. Chloride, bromide, iodide, cyanide, etc. ions displace the steady-state potentials of mercury towards negative values, which must influence the rate of the anodic oxidation of mercury. Bagotskaya[15] notes that the anodic oxidation of mercury is reversible. Accordingly, the polarisation arising under these conditions is of a purely concentration type. Therefore the relation between the anodic mercury dissolution current and the potential must be represented by the equation

$$\varphi = \varphi_0 = \frac{RT}{nF} \ln \frac{I_{Hg}}{(Id)_{Hg}},$$

where φ is the standard potential of the mercury electrode at unit concentration of mercuric ions and Id is the anodic diffusion current of mercury.

Bagotskaya calculated the potential shift in the presence of various anions from the above formula having measured the anodic currents for mercury under these conditions.

The limiting mercury oxidation current depends not only on the nature of the anion but also on its concentration, which serves as a basis for its quantitative determination[32].

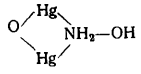
The polarisation phenomena at the dropping mercury electrode have also been investigated by Micka[33].

The kinetics of the anodic oxidation of mercury have been investigated by Elwakkad et al.[34], who demonstrated the validity of the kinetic equation

$$\partial n = AK \times \exp \frac{\alpha \varphi z F}{RT}$$

for low anodic current densities (∂n is the number of mercury atoms dissolving during time t).

The anodic oxidation of mercury in alkaline solutions has also been described[35-38]. The general conclusion that the primary product of the electrode reaction is mercuric oxide was reached. This hypothesis is supported by the finding that the mercury potential found by extrapolating the $E-t$ curves to $t = 0$ is +0.31 V and corresponds to the equilibrium potential of the Hg–HgO system. It is also interesting to note that the potentials of mercury in alkaline solutions containing suspensions of Hg_2O, HgO, and $Hg_2O.NH_2OH$ are similar. This suggests that here the potential-determining system is Hg–HgO. Then mercurous oxide and the amino-compound can be regarded as consisting of mercuric oxide and metallic mercury. Indeed X-ray diffraction analysis of "mercurous oxide" shows that this compound consists of mercuric oxide and finely dispersed metallic mercury. The amino-compounds formed when ammonia reacts with mercuric nitrate and mercurous nitrate do not have the cyclic structure



but are represented by the formula $HgO.Hg.NH_2OH$ and therefore they include mercuric oxide in their composition.

2. Kinetics of Exchange Reactions at the Mercury Electrode at Equilibrium Potentials

Measurements of the rate exchange in the system

$$Hg_2^{2+} + 2e \rightleftarrows 2Hg^0$$

at the equilibrium potential have been made by means of various non-steady-state methods[39-41]. The measurements have shown that the exchange current density for this process is high (0.4 A cm^{-2}). The authors of the investigation disregarded the ψ_1 potential because the measurements were made at a high concentration of an indifferent electrolyte. In the absence of such an electrolyte the ψ_1 potential cannot be neglected. Losev took the ψ_1 potential into account in his investigations[42-44].

According to present views, the electrochemical oxidation of a metal can take place in stages with comparable or different rates in the individual stages. It is believed that the slow stage in the oxidation of metallic mercury is $Hg_2^{2+} - 2e \rightarrow 2Hg^{2+}$, whose rate in fact determines the rate of the entire process.

The exchange currents in the system $Hg–Hg_2^{2+}$ in solutions of mercurous perchlorate, mercurous nitrate, and mercurous fluoride have been measured by the radioactive tracer method[42-44]. The exchange current was found to be 0.1 A cm^{-2}. The linear relation between the exchange current and the concentration of mercury ions in solution is thought to be evidence that the rate of the overall process is limited by diffusion. Therefore the observed exchange currents do not characterise the true rate of the electrochemical stage but the rate of diffusion of mercury ions in solution.

Losev's data are inconsistent with the results of French investigators[45-47]. The latter found that the rate of exchange is almost independent of the concentration of mercurous ions in solution and suggested that the rate of exchange is influenced by the rate of migration of mercury ions through the interface with their subsequent rapid hydration in solution and exchange by the reaction

$$Hg(aq) + Hg^{2+} \rightleftarrows Hg_2^{2+}.$$

It is believed that Hg_2^{2+} ions undergo disproportionation and the exchange takes place between hydrated atoms of metallic mercury and mercuric ions in solution.

IV. REDUCING PROPERTIES OF MERCURY

It has been established in practice that mercury has a reducing effect on a relatively large number of ions. As early as 1842, Schaffhäutel[48] showed that mercury is oxidised in the reaction with iron(III) in hydrochloric acid solution with formation of ferrous chloride and calomel. Later Borar[49] investigated the effect of mercury on certain oxidising agents and observed that their reduction is accelerated with increasing concentration of hydrochloric acid and on heating.

MacCay and Anderson[50] investigated the reduction of iron(II) with mercury and established that the reaction is quantitative. Later they studied the reduction of vanadic acid with mercury. Subsequently MacCay[51,52] discovered the conditions for the quantitative reduction of pentavalent antimony to the trivalent state. Furman and Murray[53] investigated the reduction of oxygen with mercury in hydrochloric acid solution and observed the evolution of hydrogen peroxide in this process. They also studied the reduction of molybdenum(VI) and established that the reaction leads to the formation of tri- or penta-valent molybdenum (depending on the concentration of hydrochloric acid) and calomel. Holtje and Geier[54] confirmed the above data concerning the effect of the concentration of hydrochloric acid on the extent of reduction of molybdenum(VI).

On the basis of these results, Syrokomskii and Klimenko[55] proposed a method for the determination of molybdenum in the presence of vanadium involving the reduction of molybdenum(VI) with metallic mercury.

Burriel-Marti et al.[56] studied the effect of ions forming complexes with mercury on the reducing properties of the latter and established that the presence of such ions leads to an enhancement of the reducing capacity of mercury.

According to Suranova[57], mercury reduces tungsten(VI) quantitatively to the pentavalent state.

Speranskaya and Kozlovskii[58] made a quantitative study of the reduction of a number of ions [copper(II), iron(III), selenium(IV), tellurium(IV), molybdenum(VI) etc.] with metallic mercury in different media. The experiments showed that in non-acidified solutions mercury is capable of reducing persulphate and molybdate. Other ions are reduced only in acid solutions (hydrochloric or sulphuric acid) containing added chloride.

The above data suggest that mercury is reactive with respect to many ions. In this connection, one may expect that ions interact with mercury during their electrochemical reduction at a mercury cathode.

The degree of participation of cathodic mercury in reactions of the above type can be assessed on the basis of kinetic characteristics. However, it should be noted that the kinetics and mechanism of these reactions have not been investigated. Nevertheless, having at their disposal empirical data concerning the possibility of the interaction of metallic mercury with ions undergoing polarography, some investigators have incorrectly interpreted the nature of polarographic waves[59-61]. A correct understanding of these questions requires a detailed study of the kinetics and mechanism of the reactions of metallic mercury with various ions.

The problems of the kinetics of the reactions of mercury with certain ions have been discussed[62-65].

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Non-adiabatic Processes of Energy Transfer in Gases

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The present review examines general methods for constructing the adiabatic electronic functions of molecular systems produced by binary collisions of atoms and molecules in gases. Mechanisms of energy transfer accompanying the collision of electronically excited atoms and molecules are discussed on the basis of the selection rules for non-adiabatic interactions and models of non-adiabatic coupling. These mechanisms are classified according to the amounts of electronic energy transferred on collision and according to the distances at which transfer takes place between the electronic states of the colliding species. The quenching of the electronically excited states of the atoms is brought about by close approach of the colliding species, and the probability of transitions and the corresponding cross-section depend in decisive fashion on the characteristics of the electronic functions of the system of two interacting species. Transitions between the components of the fine structure of the atomic terms take place at large distances, and the cross-section can be interpreted in terms of the characteristics of the non-excited functions for the interacting species. Transitions between the vibrational levels of molecules with incomplete electronic sub-levels are determined by vibronic or spin-orbital interaction in a given electronic configuration. The bibliography contains 62 references.

CONTENTS

Introduction 716
1. Adiabatic basis 716
2. Non-adiabatic coupling and the selection rules 717
3. Models of non-adiabatic coupling 718
4. Transfer of large amounts of electronic energy 719
5. Transfer of small amounts of electronic energy 721
6. Transfer of vibrational energy 722

INTRODUCTION

The recent progress in theoretical and experimental studies of elementary processes in the gaseous phase makes possible a detailed interpretation of the mechanisms of molecular collisions leading to energy exchange and to redistribution of the particles. Many processes take place through excited electronic states and their description requires introduction of the theory of non-adiabatic transitions. The present paper examines various processes of energy transfer involving atoms and diatomic molecules under the conditions in which the kinetics of reactions in the gaseous phase are usually studied. These processes are also used to illustrate the achievements of the theory of non-adiabatic processes.

Mention must be made of two characteristic features of molecular collisions under the above conditions. These characteristic features are extremely important, since they make it possible to simplify the overall problem considerably. On the one hand, the energy of the colliding species is so low that in the calculation of the cross-section or rate constant it is possible to consider only a small number of electronic states. On the other hand, the motion of the nuclei can still be treated quasi-classically, and very often an analysis of the classical trajectories is sufficient for the calculation of the redistribution of energy and the probability of transition between closely situated electronic terms.

1. ADIABATIC BASIS

The original approximation in the examination of the process of electronic energy transfer on slow collisions is the adiabatic approximation. There are two ways of constructing the adiabatic electronic basis: one involves the solution of the electronic wave equation for an arbitrary nuclear configuration R, whereas the other involves the solution of the equation for a configuration R_0 fixed in definite fashion[1]. Following Longuet-Higgins[2], we shall call these two possibilities the adiabatic approximation and the simple adiabatic approximation. The construction of the two bases is shown in Table 1. Here $t(r)$ and $T(R)$ denote the electronic and nuclear kinetic energy operators, $V(r, R)$ the electronic–nuclear interaction, H the complete Hamiltonian, and H_{el}, H_{nucl}, H^0_{el}, and H^0_{nucl} the partial Hamiltonians encountered in intermediate stages. Between these two limiting cases there is a whole series of other possibilities corresponding to the partitioning of the potential $V(r, R)$. For example, the usual approximation used in the calculation of the electronic structure of molecules involves making allowance for only the electrostatic contribution $V_{el}(r, R)$ to $V(r, R)$ with complete neglect of the spin-orbital interaction $V_{s.o}$. The corresponding electronic wave functions $\varphi'_n(r, R)$, which can be called the adiabatic functions of the zeroth approximation, depend parametrically on R, but the coupling between them is due not only to the operator $T(R)$ (as in the adiabatic approximation), but also to the interaction $V_{s.o}$ (as in the simple adiabatic approximation).

The exact electronic-nuclear function $\Psi_\epsilon(r, R)$ can be expanded into a series for any set, but the unknown amplitudes $A_{nE}(R)$ and $B_{nE}(R)$ must be found from an infinite system of related equations. Termination of the system, leading to the so called approximation of N-states, will generally speaking give different approximations for the complete function Ψ_ϵ in the adiabatic basis and the simple adiabatic basis. If, however, the main contribution is made only by several electronic states, the partitioning of V into V_0 and δR in appropriate fashion often makes it possible to obtain almost identical results for any basis set. This means that the N functions $\varphi_n(r, R)$ and the N functions $\varphi^0_n(r, R)$ can be regarded to a good approximation as complete sets of functions corresponding to the problem

being considered (the first simplification mentioned in the introduction).

The semi-classical approach to Ψ^a and $\Psi^{0,a}$ is obtained by replacing the nuclear functions by time-dependent exponential terms, where the classical trajectory of the nuclei is introduced $R = R(t)$ (Table 2). The choice of trajectory is a difficult problem, since it should effectively give the motion of the nuclei over several potential surfaces at once (at least in the region of strong coupling). If, however, it is possible to restrict the examination to several closely situated electronic terms, it is possible to formulate a reasonable approximation for $R(t)$ (second simplification mentioned in the introduction).

Table 1. Construction of adiabatic basis.

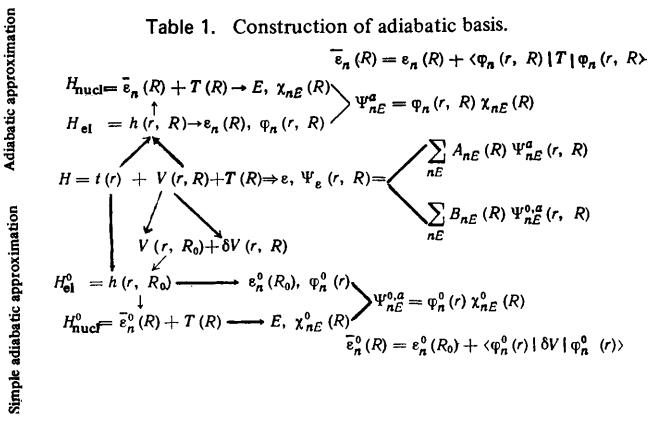

Table 2. Semi-classical approximation and non-adiabatic coupling.

Semi-classical approximation	$\Psi^a_{nE}(r, R) = \varphi_n(r, R)\chi_{nE}(R) \to$ $\to \Psi^a_n(r, R(t)) = \varphi_n(r, R(t)) \times$ $\times \exp\left[-\frac{i}{\hbar}\int^t \bar{\varepsilon}_n(R)\,dt\right]$, $R = R(t)$	$\Psi^{0,a}_{nE}(r, R) = \varphi^0_n(r)\chi^0_{nE}(R) \to$ $\to \Psi^{0,a}_n(r, R(t)) = \varphi^0_n(r) \times$ $\times \exp\left[-\frac{i}{\hbar}\int^t \bar{\varepsilon}^0_n(R)\,dt\right]$ $R = R(t)$
Non-adiabatic coupling	$\hat{C}_a = i\hbar\frac{\partial}{\partial t} = i\hbar v(t)\frac{\partial}{\partial R}$	$\hat{C}^0_a = \delta V[R(t)]$
Non-adiabatic wave function	$\Psi(r, t) = \sum_n A_n(t)\Psi^a_n(r, R(t))$, $i\hbar A_n = \sum\left\langle\varphi_n\left\|i\hbar\frac{\partial}{\partial t}\right\|\varphi_m\right\rangle \times$ $\times \exp\left[-\frac{i}{\hbar}\int[\bar{\varepsilon}_m - \bar{\varepsilon}_n]\,dt\right] A_m$	$\Psi(r, t) = \sum B_n(t)\Psi^{0,a}_n(r, R(t))$, $i\hbar B_n = \sum_n \langle\varphi^0_n|\delta V|\varphi^0_m\rangle \times$ $\times \exp\left[-\frac{i}{\hbar}\int^t[\bar{\varepsilon}^0_m - \bar{\varepsilon}^0_n]\,dt\right] B_m$

We shall not discuss here the problems associated with the calculation of the adiabatic electronic terms, and we shall mention only various useful approximations. If a comparatively large amount of electronic energy is converted into vibrational, rotational, and translational energy, the non-adiabatic coupling is usually localised at small intermolecular distances, and some information from *a priori* calculations of states is necessary. If the energy of the electronic transition is small, the interaction between the electronic terms generally takes place at large distances, and various asymptotic methods for calculating the terms can be used[3-6]. Moreover, a number of semi-empirical methods of estimating potentials, analogous to the methods used in the calculation of the probabilities of vibrational transitions[7], often prove useful.

2. NON-ADIABATIC COUPLING AND THE SELECTION RULES

The semi-classical adiabatic states corresponding to the functions Ψ^a_{nE} and $\Psi^{0,a}_{nE}$ are coupled by an interaction which was omitted in the derivation of H_{nucl} and H^0_{nucl}. The coupling operators and the semi-classical equations for the amplitudes $A_n(t)$ and $B_n(t)$ are given in Table 2. The differential equations should be integrated along the chosen trajectory, so that $\Psi_\varepsilon(r, t)$ gives the time development of the electronic functions along this trajectory. At a distance from the region of non-adiabatic interaction, $A_n(t)$ tend to constant values, and at a distance from the interaction region due to the potential δV the coefficients $B_n(t)$ also tend to constant values. These constant values of the probability amplitudes make it possible to find the system in the electronic states φ_n or φ^0_n.

In the region of non-adiabatic coupling, definite selection rules are obeyed by the electronic quantum numbers n and n'. These can be readily obtained by writing the operator C in terms of the elementary relative displacements and rotations of the axes of the system as a whole. A summary of the selection rules for a system of two colliding atoms is given in Table 3 in terms of the usual symbols[8]. Here Ω is the projection of the total momentum of the electrons on the molecular axis $\Omega = \Lambda + S_z$, and Λ and S_z are the projections of the angular momentum and the spin. The signs + and − for the Σ terms correspond to the sign on reflection of the spatial part of the wave function in a plane containing the molecular axis, and the same signs for the terms of $\Omega = 0$ correspond to the behaviour on reflection of the complete function (spatial and spin parts), whose construction made allowance for spin-orbital interaction. In this classification, for example, the ground state $^3\Sigma^-_g$ of the O_2 molecule can also be written in the form of the doublet $1_g 0^+_g$.

Table 3. Adiabatic quantum numbers and non-adiabatic selection rules for a system of two atoms.

Zeroth adiabatic approximation		Adiabatic approximation	
Perturbation: spin-orbital interaction +		radial and tangential movement of nuclei	
S	$\Delta S = \pm 1$		
S_z	$\Delta S_z = \pm 1$	Ω	$\Delta\Omega = 0\,(z)$
Λ	$\Delta\Lambda = \pm 1$ $\Big\}\ \Delta\Omega = 0$		$\Delta\Omega = \pm 1\ (R_x)$
g, u	conserved	g, u	conserved
Σ^+, Σ^-	$\Sigma^+ \longleftrightarrow \Sigma^-$	$0^+, 0^-$	$0^+ \leftarrow\!\!\!\rightarrow 0^-$

For an arbitrary triatomic system, there is only one obvious adiabatic quantum number—the nature of the reflection of the electronic function in a plane of symmetry. Any motion in the plane leaves it unchanged; this is analogous to the preservation of the sign + or − for the state of a diatomic system, when the fixed plane coincides with a

plane normal to the vector of the relative angular momentum of the nuclei. Rotation of the plane of the triatomic system will induce a change in the sign + or −, leading to mixing of all the states.

For the special case of the collision of an atom with a diatomic molecule with identical nuclear charges, it is possible to introduce a more useful classification of states, if the main contribution to the non-adiabatic coupling is made by the region where the configuration of the nuclei corresponds to C_{2v} symmetry. In this case the symbols of the irreducible representations of this point group serve as adiabatic quantum numbers. The irreducible representations and the corresponding characters are given in Table 4 for the one-dimensional representations (systems with integral spin) and two-dimensional representations (systems with half-integral spin). Here E denotes the identity operator, C_z rotation about the axis of symmetry, σ rotation in the plane of the atoms, and σ' rotation in another plane of symmetry, perpendicular to the first. Q denotes rotation by 2π, which for the two-dimensional representations is regarded as being different from E. The system of coordinates x, y, z is chosen in such a way that the z axis is directed along the axis of symmetry, and the x axis is perpendicular to the plane of the atoms.

Table 4. Adiabatic quantum numbers (irreducible representations and their characters) for a system of three atoms.

Group C_2					Group C_s		
One-dimensional representations	E	C_2	σ_v	σ_v'	One-dimensional representations	E	σ_v
$A_1(z)$	1	1	1	1	$A'(y, z, R_x)$	1	1
$B_2(y, R_x)$	1	−1	1	−1			
$A_2(w = xy, R_z)$	1	1	−1	−1	$A''(x, R_y, R_z)$	1	−1
$B_2(x, R_y)$	1	−1	−1	1			
Two-dimensional representations	E	Q	C_2, C_2Q	σ_v', $\sigma_v'Q$	σ_v', $\sigma_v'Q$	Two-dimensional representations	E	Q	σ_v, σ_v, Q
$E''\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$	2	−2	−0	0	0	$E''\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$	2	−2	0

Table 5. Non-adiabatic selection rules for a system of three atoms.

C_s		A'		A''	
	C_{2v}	A_1	B_1	A_2	B_2
A'	A_1	z	z, y R_x	R_z	R_y
	B_1	z, y R_x	z	R_x	R_z
A''	A_2	R_z	R_x	z	z, y R_x
	B_2	R_y	R_z	z, y R_x	z

It can be seen from Table 4 that there are no special selection rules for systems with half-integral spin. This is related to the fact that, of the two components of the Kramers doublet, one always has the proper symmetry. If the spin-orbital coupling is weak and can be regarded as a perturbation in the adiabatic basis of the zeroth approximation, the classification of states can be carried out in accordance with the one-dimensional representations of the point groups C_{2v} and C_s. The selection rules for the groups C_{2v} and C_s are summarised in Table 5. For C_{2v} symmetry the operation z denotes any movement of the nuclei in the fixed plane, preserving this symmetry, y represents any other movement in the fixed plane, R_z represents rotation about the axis of symmetry, R_x rotation in the fixed plane, and R_y a third rotation, affecting the orientation of the plane of the atoms in space. For C_s symmetry the operations z and y denote any movement in the plane (z and y can be pictured as the radial and tangential relative movement of the interacting species), R_x represents rotation in the fixed plane, and R_z and R_y two rotations of the plane of the atoms. The spin-orbital interaction (if it has not already been taken into account and is regarded as a perturbation) couples all the states.

These selection rules may be used below to discuss the simple elementary processes in which non-adiabatic effects are significant.

3. MODELS OF NON-ADIABATIC COUPLING

After the selection rules have been elucidated and the equations written, the problem reduces to the solution of these equations. The rapid development of electronic computers is simplifying this stage continuously. Simple models which permit an analytical solution are still playing a fundamental part, however, at least in the physical understanding of the non-adiabatic interaction of electrons and nuclei. There are a number of general approaches to the calculation of the probabilities of non-adiabatic transitions. They are all based on the application of perturbation theory either with respect to C or with respect to C^0 (Table 3).[8] If the perturbation is not small, the approximation of strong coupling, that is exact solution of a terminated system of equations, gives best results.

Of the strong coupling approximations, the so called approximation of two states is most widely used. The corresponding models are conveniently classified according to the functional dependence of the expressions adopted for the approximations $\overline{\epsilon}_1^0$ and $\overline{\epsilon}_2^0$, and also of the non-diagonal matrix element δV_{12} in the basis of the two functions φ_1^0 and φ_2^0 of the simple adiabatic approximation.

With this classification we can discuss three main types of model.

a. The linear model, in which the matrix elements in the non-adiabatic region are approximated by linear functions of the nuclear coordinates. This model was first formulated by Landau[9] and Zener[10]. Subsequent studies, published chiefly in the last five years, have extended the range of applicability of this model both for the wave description of the motion of nuclei[11-15] and for the classical description[16-19].

b. The exponential model, in which the matrix elements are approximated by exponential functions of the nuclear coordinates. The most general formulation within the framework of the semi-classical approximation was made in a paper by Nikitin[20], which yielded, in particular, the results obtained by Rosen and Zener[21], who were the first to examine the exponential model. This model was subsequently developed further[22-24].

c. The power model, in which the matrix elements are approximated by power functions of the internuclear distance R^{-n} or R^{n}. This model has been studied comparatively recently[25-27].

Finally, mention must be made of papers[28-34] in which general aspects of the theory of the non-adiabatic coupling of two states are discussed.

All the elementary processes discussed below can be related to the various models, which in turn make it possible to interpret the cross-sections or rate constants of the non-adiabatic characteristics of the interacting species.

4. TRANSFER OF LARGE AMOUNTS OF ELECTRONIC ENERGY

A simple example of the exchange of energy between electronic and translational degrees of freedom is provided by the thermal excitation and deactivation of alkali metal atoms M on collision with atoms of an inert gas X

$$M(^2S) + X(^1S_0) \rightleftarrows M^*(^2P_j) + X(^1S_0) - \Delta\varepsilon \quad . \qquad (1)$$

An early interpretation of the quenching of the fluorescence of sodium by argon[35] was based on a simplified version of the theory and was related to low-temperature experimental data[36]. Recent experiments in shock tubes[37,38] cast doubt on the low-temperature results, although in themselves they are still insufficient for determination of the values of the quenching constant, because of the large experimental errors. Up to the present, only one attempt[39] has been made to calculate the constants k_1 and k_{-1} with allowance for all possible interactions responsible for the change in the electronic state of M.

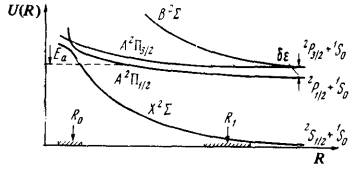

Figure 1. Lower adiabatic terms of the alkali metal atom–inert gas atom system.

As far as the adiabatic terms are concerned, non-empirical calculations have been carried out apparently only for the Li–He system[40,41], which gives the behaviour of the terms for the alkali metal–inert gas general case (Fig. 1). For heavy atoms X, however, the polarisation interaction may be so great that the activation energy E_a of process (1) will be equal to zero. Nevertheless, in order to be specific, we will consider the case for which the qualitative arrangement of the terms corresponds to the picture given in Fig. 1 ($E_a > 0$) and corresponding to a light inert gas.

The change in the electronic state of the colliding pair M and X takes place close to the internuclear distance R_0. In accordance with the usual classification, the ground electronic state of the combined system should be classified as $X^2\Sigma$. At R_0 this term is found to be close to the term of the first excited state $A^2\Pi_\Omega(\Omega = 1/2,\ 3/2)$, which has a fine structure. When $R \to \infty$, this term correlates with the atomic states $^2P_{1/2} + {}^2S$ and $^2P_{3/2} + {}^2S$. Rotation of the colliding pair mixes the states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and this is usually described as a transition from Hund's coupling case a to coupling case b. Each of the two new states in turn is split into two components as a result of non-adiabatic coupling with the close $X^2\Sigma$ state (so called Λ-splitting). Finally, radial movement induces a non-adiabatic transition, since the coupling coefficients are markedly dependent on R. Mathematically, the problem reduces to the solution of three coupled equations for $A_\eta(t)$ within the framework of the linear model first examined by Landau[9] and Zener[10]. A more exact version of the theory[14] takes account of tunneling, which is important for high activation energy or for strong spin-orbital interaction. It has been found that in the semi-classical approximation the probability of a transition can be obtained by simple summation of the fluxes for each electronic term, calculated as if there were independent coupling between each pair of terms at their point of intersection[15]. This denotes the absence of interference between the probability amplitudes for the terms $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, although the phase difference between the two points of intersection is generally small.

Thus the theory gives extremely general expressions for k_1 and k_{-1}, leaving the theoretical parameters indeterminate. The rate constants can be estimated from familiar expressions[42] with the condition that there are some indications of the magnitude of the activation energy. On the other hand, if the temperature dependence of k_{-1} were measured sufficiently accurately, the theory would make it possible to interpret reaction (1) in terms of the adiabatic characteristics of the pair M and X. This has not yet been done. The only reliable conclusion is that the exchange of electronic and translational energy on atomic collisions has a low probability[43].

Let us now consider the deactivation of excited atoms by diatomic molecules. A number of experiments show that this deactivation takes place extremely effectively[44-48]. This suggests that in these processes there is resonance between an electronic level of the excited atom and the vibrational levels of the molecule. This problem has not been examined theoretically. Apart from the very difficult problem of solving the coupled wave equations (or the corresponding time-dependent equations of the semi-classical approximation), there arises another problem, associated with the possibility that the representative point passes repeatedly through the region where the adiabatic potential surfaces intersect or approach close to one another. Even if all the quantum-mechanical interference effects are neglected, it is very difficult to take account of all the contributions to the probability of a non-adiabatic transition from different points on the two-dimensional or multi-dimensional trajectory.

One of the simplest processes of this kind

$$Na^*(^2P) + N_2(^1\Sigma_g^+,\ v=0) \rightarrow Na(^2S) + N_2(^1\Sigma_g^+,\ v \geqslant 0) \qquad (2)$$

was examined by Bjerre and Nikitin[49], and also by Bauer[50]. These workers first tried to interpret it as a non-adiabatic transition between covalent adiabatic surfaces, produced from the energy states $^2P + {}^1\Sigma_g^+$ and $^2S + {}^1\Sigma_g^+$ of the separated interacting species. These surfaces for a fixed (N–N) distance are represented qualitatively in Fig. 2 in terms of relative coordinates R and Θ (the intermolecular distance and the angle of orientation). The Figure also shows the quantum numbers of the adiabatic states in the zeroth approximation for the symmetries $C_{\infty v}$, C_{2v}, and

C_s. With reasonable assumptions regarding the interactions, however, this attempt proved unsuccessful. Following Laidler[51,52] and Mori[53], the authors supplemented the system of covalent terms with an ionic term. In the zeroth approximation there then arise three potential surfaces: the purely covalent I $[Na(^2P) + N_2(^1\Sigma_g^+)]$, the purely ionic II $\{Na^+ + [N_2(^3\Sigma_u^+)]^-\}$, and the purely covalent III

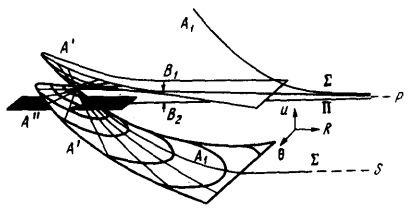

Figure 2. Lower adiabatic terms of the zeroth approximation (the spin-orbital coupling is not taken into account) for the alkali metal atom-nitrogen molecule system. The N–N distance is fixed, and the interaction with the ionic term is not taken into account.

$[Na^g(^2S) + N_2(^1\Sigma_g^+)]$. The ionic surface and the interaction matrix element $\delta V_{nn'}$, corresponding to non-adiabatic coupling between the adiabatic functions of the zeroth approximation, were calculated approximately[49] from experimental data[54] on the resonance scattering of slow electrons by N_2. The general arrangement of the surfaces for linear collision is shown in Fig. 3. Here R denotes the distance between the Na atom and the centre of the N_2 molecule, and r the interatomic distance in the N_2 molecule. The coordinates r_I, r_{II}, and r_{III} correspond to the equilibrium interatomic distances in the N_2 molecule in the corresponding

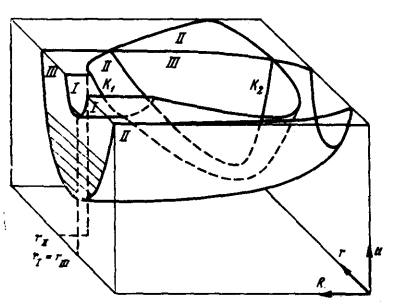

Figure 3. Lower adiabatic terms of the zeroth approximation (the interaction between the ionic term and the covalent terms is not taken into account) for the alkali metal atom-nitrogen molecule system. Linear arrangement of the atoms. Term I—excited covalent state; term II—ionic intermediate state; term III—covalent ground state.

electronic states for an infinitely large distance between the interacting pair ($R \to \infty$). The surfaces I–II and II–III intersect along the lines K_1 and K_2. If the non-diagonal elements of the interaction are taken into account, the intersections are converted into pseudo-intersections. When a certain trajectory L of the representative point reaches the lines K_1 or K_2, there is a certain probability of branching, leading to the appearance of two trajectories. The Landau–Zener formula was used to calculate the probability of the trajectory, and the trajectories were found by computer solution of the classical problem. Analysis of the trajectories made it possible to calculate the partial cross-sections and rate constants for reactions leading to a definite vibrational state v, and also led to the following general conclusions: (1) there is no indication that vibronic resonance is significant in process (2); (2) although the ionic surface shows a fairly deep minimum, the breakdown of $Na^+–N_2^-$ into $Na(^2S) + Na_2(^1\Sigma_g^+, v)$ takes place approximately in the time of one collision. This means that, for effective energy transfer, the formation of a long-lived intermediate complex is not essential, although it is possible that in other instances the formation of a complex facilitates the energy redistribution[55]; (3) the distribution with respect to vibrational levels is very sensitive to the magnitude of the splitting of the electronic terms of the zeroth approximation. Nevertheless, for process (2) a "reasonable" distribution function corresponding to the maximum at $v = 2$ and 3 was found. This conclusion shows qualitative agreement with experiment. An example of the calculated distribution function for the N_2 molecule with respect to the vibrational states is given in Fig. 4.

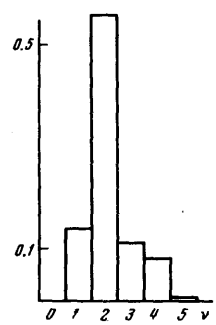

Figure 4. Example of the distribution function with respect to vibrational states for an N_2 molecule excited in the non-adiabatic process (2).

These non-adiabatic transitions take place between electronic terms with the same symmetry. The electronic transition is induced by the movement of the atoms in the plane (coordinates z and y from Table 4) and, to a much smaller extent, by rotation in the plane (R_x) and by spin-orbital interaction.

Another interesting example is provided by the reactions

$$Hg^*(^3P_0) + CO(^1\Sigma^+,\ v=0) \rightarrow Hg(^1S_0) + CO(^1\Sigma^+, v>0), \quad (3a)$$

$$Hg^*(^3P_0) + NO(^2\Pi,\ v=0) \rightarrow Hg(^1S_0) + NO(^2\Pi,\ v>0) \quad (3b)$$

of which the first is less effective than the second[46,47]. In the case of mercury the spin-orbital interaction is so great that it must be included in the electronic Hamiltonian. The initial state in process (3a), produced from $^3P_0 + {}^1\Sigma^+$, should then be classified as the one-dimensional representation A'' of the point group C_s of a system of three atoms. The final state $(^1S_0 + {}^1\Sigma^+)$ corresponds to the symmetry A',

since the transition (3a) is induced by rotation of the complete system by R_z or R_y. For process (3b) the initial and final states correspond to the same symmetry—both belong to the two-dimensional representation E''. This allows the movements in the plane (z and y) to be active in inducing transitions. These two mechanisms provide a qualitative explanation of the difference in the efficiencies of electronic deactivation on collisions with molecules having complete or incomplete electronic sublevels. We shall return to this problem below in connection with the transfer of vibrational energy.

5. TRANSFER OF SMALL AMOUNTS OF ELECTRONIC ENERGY

If an electronic transition takes place between two close energy states as a result of a collision, the cross-section for this process will be large. The probability of a transition depends on the magnitude of the minimal splitting between the adiabatic terms $\Delta\epsilon^{min}$, on the effective dimensions a of the region of the transition, and on the velocity of the nuclei in this range v. The parameter determining chiefly the magnitude of the probability of a transition is the ratio $\xi^{min} = \Delta\epsilon^{min}a/\hbar v$ (the so called Massey parameter), the probability of the transition being exponentially small for $\xi^{min} \gg 1$. Within the framework of the Landau-Zener model, applicable for electronic deactivation, $a \simeq \Delta\epsilon^{min}/\Delta\epsilon\alpha$, where $\Delta\epsilon$ is the energy of the reaction and α the orbital exponent of the outer electron. We thus obtain:

$$\xi^{min} \simeq \frac{(\Delta\varepsilon^{min})^2}{\hbar\alpha v\Delta\varepsilon} = \left(\frac{\Delta\varepsilon^{min}}{\Delta\varepsilon}\right)^2 \xi^{\infty},\ \xi^{\infty} = \frac{\Delta\varepsilon}{\hbar\alpha v}\ , \qquad (4)$$

the linear model being applicable only for the following conditions [35]

$$\xi^{\infty} \simeq \frac{\Delta\varepsilon}{\hbar\alpha v} \gg 1,\ \frac{\xi^{min}}{\xi^{\infty}} \simeq \frac{(\Delta\varepsilon^{min})^2}{\Delta\varepsilon^2} \ll 1\ . \qquad (5)$$

If in a non-adiabatic process one of the inequalities (5) is not fulfilled, the linear model should be replaced by a more general model.

An illustrative example is provided by the reactions

$$M^*(^2P_{1/2}) + X(^1S_0) \rightarrow M^*(^2P_{1/2}) + X(^1S_0) + \delta\varepsilon \qquad (6)$$

in which the collisions induce mixing of the components of the multiplet of the fine structure in the excited atoms of the alkali metal. These processes have been studied experimentally in fairly complete detail, and an extremely marked change in cross-sections was observed in the order M = Na, K, Rb, and Cs.[56] For all processes of this kind, we have $\xi^{\infty} \simeq \xi^{min}$ and under the conditions of the experiment the relationship $\xi^{min} \geq 1$ is satisfied. The mechanism of the change in quantum number is clear from Fig. 1. Mixing takes place at fairly large distances R_1 and, in accordance with Table 3, is brought about by radial movement and rotation, the former making the chief contribution. The theory based on non-linear models[57,58] predicts, in agreement with experiment, a variation in cross-section from the large value of 10^{-14} cm^2 for the Na*–He pair to the extremely small value 10^{-21} cm^2 for the Cs*–He pair. If we make the reasonable estimate $\Delta\epsilon^{min} \simeq \delta\epsilon$, it can be seen that

$$\xi^{min}_{quench} \simeq \left(\frac{\delta\varepsilon}{\Delta\varepsilon}\right)^2 \xi^{min}_{mix}\ . \qquad (7)$$

Thus even if intramultiplet transitions have a low probability ($\xi^{min}_{mixing} \gg 1$), electronic deactivation may be effective, since $\delta\epsilon/\Delta\epsilon \ll 1$. The true efficiency of deactivation of the excited state of course depends on the magnitude of the activation energy (see previous section).

If the inert gas atom is replaced by an inert diatomic molecule $X_2(^1\Sigma_g^+)$, we can expect an increase in the cross-section for the mixing of the components of the multiplet as a result of the contribution of the rotational and vibrational degrees of freedom to the overall process. Under these conditions, an increase in cross-section as a result of vibronic resonance is extremely probable, since resonance leads to a significant change in the selection rules for the vibronic spectrum relative to the selection rules in the independent electronic and vibrational spectra. A reaction of type (6) with replacement of X by X_2 is not very illustrative in this connection, since all the vibronic terms belong to the same two-dimensional representation E'', so that there are no special selection rules.

The following reactions provide a clearer example:

$$Hg^*(^3P_1) + Ar(^1S_0) \rightarrow Hg^*(^3P_0) + Ar(^1S_0) + \delta\varepsilon \qquad (8a)$$

$$Hg^*(^3P_1) + N_2(^1S_0) \rightarrow Hg^*(^3P_0) + N_2(^1\Sigma_g^+,\ v=1) + \delta\varepsilon - \hbar\omega\ . \qquad (8b)$$

The correlation diagrams for the adiabatic terms of the Hg*–Ar pair are given in the right-hand side of Fig. 5. It can be seen from Table 3 that process (8a) is due to rotational (R_x) mixing of the molecular states $\Omega = 0^-(^3P_0)$ and $\Omega = 1(^3P_1)$. The probability of the process is extremely small, since the Massey parameter is large (small exponential factor), and the terms have different symmetries (additional small pre-exponential factor). It is known from experiment that reaction (8a) proceeds very slowly[43]. On the other hand, reaction (8b) proceeds very rapidly, almost in every collision. This fact cannot be attributed simply to a decrease in the Massey parameter, in replacing $\delta\epsilon$ by $\delta\epsilon - \hbar\omega$. The true reason for the increase in efficiency can be seen from the correlation diagram.

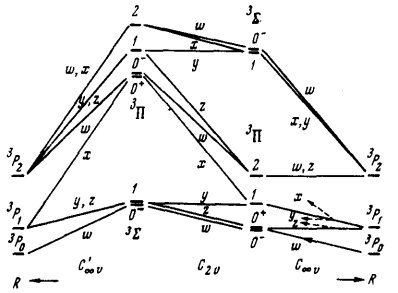

Figure 5. Correlation diagram of adiabatic terms of the system $^2P_j + {}^1S_0$ ($C_{\infty v}$ symmetry) and the system $^3P_j + {}^1\Sigma_g^+$ (C_{2v} and C_s symmetry). The symbols x, y, z, and w correspond to those of Table 4.

For system (8b) with a fixed vibrational quantum number, there are two relative displacements in the plane (z and y). We shall restrict ourselves to a discussion of a specially selected section of the system of two-dimensional adiabatic potentials, by following throughout a path in which the system retains the formal symmetry $C_{\infty v}$ and C_{2v}. Along this path we shall vary the three interaction parameters V_x, V_y, and V_z, which correspond to the three electronic states A_1, B_1, and B_2, produced from the spin-free P state. This section is determined as follows (from right to left in Fig. 5).

1. Free species:

$$V_x = 0,\ V_y = 0,\ V_z = 0.$$

2. $C_{\infty v}$ symmetry:

$$V_x = 0,\ V_y = 0,\ 0 < V_z < V_0.$$

3. C_{2v} symmetry:

$$V_x = 0,\ 0 < V_y < V_0,\ V_z = V_0\ .$$

4. $C_{\infty v}$ symmetry:

$$0 < V_x < V_0,\ V_y = V_0,\ V_z = V_0\ .$$

5. Free species displaced along the energy scale:

$$V_x = V_0,\ V_y = V_0,\ V_z = V_0\ .$$

The broken line shows the splitting of the levels, degenerate for $C_{\infty v}$ symmetry, if the section is defined in a slightly different way (stage 3 replaced by 3a). In this case we have the following situation.

3a. C_{2v} symmetry:

$$V_x = 0,\ 0 < V_y < V_0,\ 0 < V_z < V_0.$$

Decrease in symmetry from C_{2v} to C_S does not lead to further splitting—the only change is in the adiabatic mixing of the states of the same symmetry.

The arrangement of the vibronic terms for states with different quantum numbers v is obtained by superposition of diagrams of this kind with a displacement by $\hbar\omega$. This leads to intersection of the terms. Some of them are converted into pseudo-intersections, after the interaction δV is taken into account. Detailed study[59] shows that reaction (8b) induces combined movement along the coordinates z and y (radial and tangential relative movement of the interacting species), which mixes two states of symmetry A'', correlating with the states $^3P_1 + {}^1\Sigma_g^+$, $v = 0$, and $^3P_0 + {}^1\Sigma_g^+$, $v = 1$ of the interacting pair. The main contribution is made by the configuration close to the configuration of an isosceles triangle. For C_{2v} symmetry, these two states are classified as w (or A_2) and x (or B_2). These two terms have different symmetry and intersect the symmetric configuration; the two vibronic A'' states mentioned above refer to an adiabatic surface in the form of a double cone. It is this feature—the intersection of two terms with the same symmetry in a single point—which provides the fundamental difference between the atom–molecule process (8b) and the atom–atom process (8a). The rotation R_x also makes a contribution to the transition (8b), but its effect is relatively small, whereas for (8a) the rotation R_x is the only perturbation.

6. TRANSFER OF VIBRATIONAL ENERGY

In the previous sections it was shown that the removal of the degeneracy of the electronic state of one of the interacting species plays a large part in the mechanism of the exchange of electronic energy. By analogy, it may be expected that the transfer and exchange of vibrational energy will be different for interacting species with complete or incomplete electronic sublevels. This is in fact the case[60,61]. The physical picture is as follows. The intermolecular interaction leads to splitting (other than the Kramers doublet) of the degenerate electronic term of one of the interacting species, and at a certain distance this splitting becomes equal to the vibrational quantum. As a result of vibronic resonance, there is a high probability of energy exchange between the vibrational and translational movement.

Let us consider first the collision of a diatomic molecule with an inert gas atom, leading to the vibrational transition $v = 1 \rightarrow v = 0$. If the molecule is in a non-degenerate electronic state, both vibronic states correspond to symmetry A' (or A''). In accordance with Table 5, the transitions are then brought about by the perturbations z, y, and R_x. The first two represent relative movement and rotation, and their contribution depends on the corresponding reduced masses. Overall rotation in the plane does not make a significant contribution to the probability of the transition. If, however, the molecule is in, for example, a Π state, states of both types of symmetry A' and A'' are produced on interaction. With allowance for the spin-orbital interaction, the term $^2\Pi$ is split into components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and the possible intersections of the terms $^2A'$ and $^2A''$ are converted into pseudo-intersections. The system of vibronic terms produced in this way is shown in Fig. 6. If the spin-orbital interaction between the vibronic states is small, it can be regarded[59] as the reason for the transition, together with the rotations R_y and R_z.

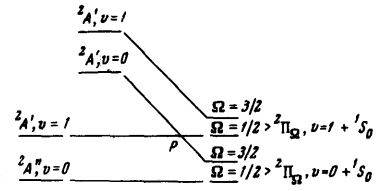

Figure 6. Correlation diagram of vibronic adiabatic terms of the system $^2\Pi_\Omega$; $v + {}^1S_0$ (or $^1\Sigma_g^+$).

Two possible paths of the vibrational transition in the above system are:

the adiabatic path

$$^2\Pi_{1/2}, v = 1 \rightarrow P \rightarrow {}^2A'', v = 1 \rightarrow {}^2A', v = 0 \rightarrow {}^2\Pi_{1/2}, v = 0, \quad (9)$$

the non-adiabatic path

$$^2\Pi_{1/2}, v = 1 \rightarrow P \rightarrow {}^2A'', v = 1 \rightarrow P \rightarrow {}^2\Pi_{1/2}, v = 0 \rightarrow {}^2\Pi_{1/2}, v = 0.$$

For two diatomic molecules, the arrangement of the vibronic states will be more complicated, but the general features are retained. As an illustration, we give here three reactions which have now been fairly well studied:

$$O_2(v = 1) + O_2(v = 0) \rightarrow O_2(v = 0) + O_2(v = 0) + \hbar\omega, O_2(^3\Sigma_g^-), \quad (10a)$$

$$NO(v = 1) + NO(v = 0) \rightarrow NO(v = 0) + NO(v = 0) + \hbar\omega, NO(^2\Pi_\Omega), \quad (10b)$$

$$N_2(v = 1) + N_2(v = 0) \rightarrow N_2(v = 0) + N_2(v = 0) + \hbar\omega, N_2(^1\Sigma_g^+), \quad (10c)$$

Of these processes, only reaction (10b) relates to interacting species with electronic terms quasi-degenerate in space. As a result of the interaction, the states of the system $NO(^2\Pi) + NO(^2\Pi)$ move apart as the interacting species approach. In the system $N_2(^1\Sigma_g^+) + N_2(^1\Sigma_g^+)$ splitting does not take place at all, and in the system $O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$ electrostatic interaction cannot alter the fine structure of the spatially non-degenerate terms. Detailed examination shows that the main contribution to process (10b) is made as a result of spin-orbital interaction between the lower states $^1A'$ and $^3A''$, correlating with the states $^2\Pi + {}^2\Pi$ of the free species[60]. The Massey parameter for the adiabatic path, as for process (9), is greater than that for the non-adiabatic path, but the interaction is stronger for the adiabatic path (since states with the same symmetry

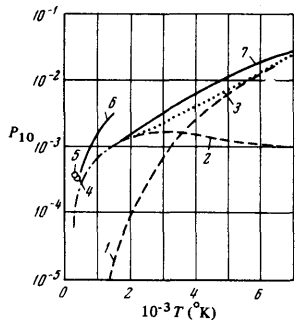

Figure 7. Adiabatic (*1*) and non-adiabatic (*2*) contributions to the total (*3*) probability P_{10} of the vibrational transition $v = 1 \rightarrow v = 0$ for the NO molecule. The points and curves *4–7* correspond to different experimental data[62].

are taking part). Thus these two paths compete, and at low temperature the non-adiabatic process predominates. Thus at room temperature the rates of processes (10a) and (10c) are smaller by three or four orders of magnitude than the rate of process (10b). This competition of the two mechanisms is shown in Fig. 7, taken from Wray's paper[62].

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The "Memory" Effect in Semiconductor Adsorbents and Catalysts during Radiation†

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CONTENTS

I. The "memory" effect under various forms of irradiation 724
II. "Memory" associated with a shift in the electronic equilibrium 725
III. "Memory" associated with a disturbance of the electronic equilibrium 726

I. THE "MEMORY" EFFECT UNDER VARIOUS FORMS OF IRRADIATION

This review is concerned exclusively with semiconductors, but all the statements to be made can be generalised to include dielectrics. There is no difference in principle between semiconductors and dielectrics other than the scale used to represent the energy spectrum. By expanding the spectrum we progress from semiconductors to dielectrics, whereas by compressing it we convert dielectrics into semiconductors.

The term irradiation will be used in the widest possible sense. It will refer to electromagnetic radiation, including visible and ultraviolet light, X-rays, and gamma rays. It will refer also to corpuscular radiation, including bombardment with neutrons, electrons, protons, and alpha particles. In every case, the material experiences a flux of energy from outside. Changes induced in solids by these various types of radiation often have a great deal in common.

Radiation is known to affect several of the properties of a semiconductor. First and foremost, it affects the electrical and optical properties of the material: the magnitude, temperature dependence, and sometimes even the type of the conductivity are affected; absorption bands are shifted; the spectrum, the intensity, and the decay rate of the luminescence are altered. The mechanisms underlying changes in all these properties, and involving the formation of radiation defects in the semiconductor, are fairly well understood (at least, qualitatively).

The mechanism of the influence of irradiation on the adsorption and catalytic properties of semiconductors, with which the present article is concerned, is very much less well understood. Irradiation often causes profound changes in the properties of a semiconductor. A semiconductor having little or no catalytic activity often emerges from this operation as an active catalyst. A semiconductor showing negligible adsorption is often converted into a good adsorbent by irradiation. In spite of numerous experimental investigations, the mechanism of these changes remains obscure. Some of the relevant problems will be discussed in this article.

Workers investigating the effect of irradiation on the adsorption and catalytic properties of semiconductors are faced with a two-fold problem. On the one hand, an understanding of the mechanism of the phenomenon is required, and on the other hand we must learn to control the properties of a semiconductor by modifying them to the required extent and in the appropriate direction by means of irradiation.

† Paper presented to the Miller conference on radiation chemistry (Warsaw, September, 1967).

As soon as the problem is formulated in terms of the use of irradiation as a tool for controlling the properties of a semiconductor, one is faced with the problem of the "memory" of the semiconductor: how long will the changes produced by irradiation persist in the semiconductor, or in other words, how long will the semiconductor "remember" the irradiation? The answer to this question varies from case to case. The problem of the memory of a semiconductor is the focal point of the present article.

A semiconductor sometimes forgets the irradiation instantaneously, immediately after the irradiation is removed. This is one extreme case. The opposite extreme is also possible, the "memory" of the irradiation remaining indefinitely in the semiconductor. But we are often faced with the intermediate, and more general, case of a semiconductor which remembers the irradiation for a finite time and gradually forgets it. We shall discuss all three cases.

The first case is encountered when the effect of irradiation is to produce ionisation directly, i.e. to generate non-equilibrium current carriers in the semiconductor. In this case the semiconductor remembers the irradiation only as long as it is exposed to it. The inner photoelectric effect produced by visible or u.v. light, by X-rays, or by gamma rays is a case in point. The irradiation gives rise to a disturbance of the electronic equilibrium in the semiconductor, and when the irradiation is interrupted the semiconductor usually reverts to its original equilibrium state very rapidly and almost instantaneously. Some exceptions to this rule will be discussed below.

The other limiting case (of a semiconductor which, once exposed to irradiation, remembers the event forever) is observed when the irradiation induces a nuclear reaction in the semiconductor. In this case the irradiation has the effect of increasing the impurity content of the semiconductor by converting normal lattice atoms into foreign atoms. This process is irreversible, and is accompanied by a shift in the electronic equilibrium. We note that both limiting cases can occur together when the products of the nuclear reaction are radioactive, and the semiconductor remains exposed to its own radiation.

Lastly, in the more general case, the memory of the irradiation remains in the semiconductor for a certain time and then gradually disappears. This case arises when the radiation, without actually changing the chemical composition of the semiconductor, leads to the appearance of structural defects, i.e. produces additional (radiation-induced) "disorder" in the lattice. This effect results in a shift of the Fermi level, i.e. in a displacement of the electronic equilibrium, which persists under these conditions. This effect is wholly equivalent to the introduction of impurities into the semiconductor, since the terms

"defect" and "impurity" are synonymous in the language of semiconductor physics. All structure-sensitive properties of the semiconductor must immediately find a new level as a result of the effect.

However, the radiation-induced disorder resulting from illumination is gradually re-absorbed when illumination is discontinued. The process can be accelerated by heating. In other words, by heating the semiconductor we compel it to forget the irradiation more quickly. The "impurities" created in the semiconductor by this process eventually disappear: this property distinguishes them from the impurities formed as products of a nuclear reaction.

Thus, by observing the "memory" of a semiconductor, i.e. by noting how quickly the semiconductor forgets its irradiation, we can identify to some extent the events taking place in the semiconductor during irradiation. In general, irradiation produces more or less reversible changes in the semiconductor. Sometimes, when the irradiation produces unfavourable changes in the semiconductor, we shall endeavour to make these changes easily reversible; conversely, when irradiation is applied in order to control the properties of the semiconductor, we shall be concerned with the stability of the changes.

Thus, irradiation affects the semiconductor in two ways. Firstly, it gives rise to structural defects and to chemically foreign impurities in the semiconductor. Secondly, it induces direct ionisation. In the first case we are dealing with a shift in the electronic equilibrium to what can be treated as a new equilibrium situation. In the second case we are dealing with a disturbance of the electronic equilibrium with generation of non-equilibrium carriers. In the first case the semiconductor remembers the irradiation forever, or for more or less extended periods. In the second case it forgets the irradiation almost immediately.

II. "MEMORY" ASSOCIATED WITH A SHIFT IN THE ELECTRONIC EQUILIBRIUM

We shall consider here the case of a shift in the electronic equilibrium as a result of irradiation.

We must stress, first of all, that the adsorption and catalytic properties of a semiconductor, which are our main concern, are usually related to properties of an entirely different kind: to the work function and electrical conductivity of the semiconductor. This statement is based on a large fund of experimental evidence. The adsorption capacity and catalytic activity of a semiconductor (on the one hand), and its work function and electrical conductivity (on the other hand), are linked by well defined correlations in most cases. The origin of this correlation is made clear by the electronic theory of chemisorption and catalysis [1].

A displacement of the electronic equilibrium (or in other words a shift of the Fermi level) results first of all in a change of the work function and carrier concentration of the semiconductor.

According to the electronic theory, an increase in work function (i.e. an increase in the concentration of free holes and a decrease in the concentration of free electrons, or in other words an increase in the contribution of holes and a decrease in the contribution of electrons to electrical conduction) is accompanied by an increase in the adsorption capacity of the surface towards donor molecules and, conversely, by a decrease in the adsorption capacity of the surface towards acceptor molecules.

As regards the catalytic activity, i.e. the rate of catalytic reactions taking place at the surface, all reactions can be divided into two classes from the standpoint of the electronic theory. One class includes the reactions which are accelerated by an increase in the work function. These reactions, called donor reactions, are accelerated by holes and retarded by electrons. Their rate varies in the same sense as the hole conduction, and in the opposite sense to the electronic conduction. The other class (acceptor reactions) includes those reactions whose rate is increased by lowering the work function. These reactions are accelerated by electrons and retarded by holes. In this case the catalytic activity varies in the same sense as the electronic conduction and in the opposite sense to the hole conduction.

Thus, changes in the electrical conductivity of a semiconductor give rise to changes in the adsorption capacity and in the catalytic activity, the changes being in the same sense or in the opposite sense depending on the nature of the semiconductor (p-type or n-type), on the nature of the adsorbed gas (donor or acceptor gas), and on the nature of the reaction (donor or acceptor reaction). The electronic theory is in no way concerned — and this must be stressed — with the cause of the conductivity changes. The correlation applies irrespective of the agency responsible for the shift of the electronic equilibrium. It could be an impurity added to the semiconductor: indeed, we know that changes in conductivity, accompanied by changes in adsorption capacity and in catalytic properties, can be brought about by doping the semiconductor. Alternatively, the agency could be irradiation. Hence, we are able to predict the effect of irradiation on the adsorption capacity and on the catalytic activity from the changes in electrical conductivity caused by the irradiation.

This general conclusion of the electronic theory can be illustrated by considering the decomposition of alcohols, for which two alternative mechanisms are known: dehydrogenation and dehydration. Let us consider first the dehydrogenation reaction. This, in the terminology of the electronic theory (see Section 6b in Ref. 1), is a typical acceptor reaction, accelerated by high concentrations of electrons and by low concentrations of holes in the semiconductor.

Evidence for the acceptor nature of this reaction comes from various sources. Thus, Zhabrova and coworkers [2], in their study of the dehydrogenation of isopropanol on zinc oxide, studied the changes in catalytic activity and in work function resulting from the addition of various impurities (both donors and acceptors) to the catalyst. A distinct correlation was observed: the lower work function, the greater was the activity. In an earlier investigation, Myasnikov and Pshezhetskii [3] examined the same reaction on a zinc oxide surface covered with chemisorbed oxygen, which behaved as a surface impurity in these experiments. Under the influence of oxygen, the electrical conductivity and the catalytic activity were found to decrease together. Since zinc oxide is an n-type semiconductor, conductivity and activity changes occurring in the same sense indicate that the dehydrogenation of an alcohol is an acceptor reaction.

Tsetskhladze and Kalandadze [4] made simultaneous observations of the effect of irradiation on the electrical conductivity and on the catalytic activity. The electrical conductivity of their specimens of cuprous oxide was increased by several orders of magnitude by gamma irradiation. The changes were relatively long-lived, and were probably caused by atomic displacements induced by the irradiation. The same samples were used as catalysts for the dehydrogenation of ethanol. Since cuprous oxide is a typical p-type semiconductor, and the dehydrogenation reaction (as indicated above) is a typical acceptor reaction, the activity could be expected to vary in a sense opposite to

that of the conductivity. This expectation was confirmed: according to the measurements of Tsetskhladze and Kalandadze, the reaction was strongly inhibited by previous irradiation.

Let us now turn to the dehydration reaction. It is usually assumed that this reaction takes place by an acid–base mechanism, which presupposes the presence of mobile hydrogen (Brønsted acid) on the surface. With oxide and hydroxide catalysts the mobile hydrogen is provided by OH groups, and the reaction ceases when these groups are removed from the surface. This mechanism, in every way analogous to the mechanism of homogeneous acid–base catalysis, is believed to exclude any correlation between the catalytic and the electronic properties of the catalyst. Yet, correlations have been observed by many workers and can hardly be dismissed as fortuitous.

Thus, Zhabrova and coworkers (see above[2]) doped their zinc oxide with sodium (donor) and sulphur (acceptor) impurities, and found that the work function was decreased by the former and increased by the latter. At the same time, they measured the catalytic activity towards the dehydration of isopropanol, and found that addition of sodium inhibited the reaction whereas addition of sulphur increased the reaction rate. Since the work function and the catalytic activity vary in the same sense, this reaction is of the donor type from the standpoint of the electronic theory.

Indeed, the dehydration of alcohols can be classified as a donor reaction in the terminology of the electronic theory both in the case of a purely electronic and in the case of an acid–base mechanism (as can be demonstrated). This is because the participation of positive holes is essentially implied in both the purely electronic mechanism (see Section 6b of Ref. 1) and in the acid–base mechanism, in which the catalyst and the reacting molecule exchange a proton with formation of an oxonium ion and subsequently of a carbonium ion as intermediates[5].

Spitsyn and coworkers[6] studied the dehydration of decanol $C_{10}H_{21}OH$ on tungsten disulphide WS_2. The samples had a stoichiometric defect of sulphur; as expected, they were found to be n-type by measurements of thermo-e.m.f. Special preliminary experiments confirmed the absence of hydrogen or hydroxyl groups on the surface. Thus, the acid–base mechanism (in the Brønsted sense) was excluded, and yet dehydration took place at appreciable rates.

The specimen was then placed in a nuclear reactor, where it was irradiated with slow neutrons. Radioactive isotopes of tungsten and sulphur were formed, so that the material remained exposed to internally generated and slowly decaying beta and gamma radiation after the neutron bombardment was stopped. The electrical conductivity of the sample was appreciably lowered by this treatment, and remained lower than the conductivity of the non-irradiated material over the whole of the experimental temperature range (from 20 to 350°). This fact alone is proof that the effect of the radiation in this case cannot be simple ionisation: were it not so, the radiation could only lead to an increase in conductivity.

The catalytic activity was measured at the same time as the electrical conductivity on the same specimens. In view of the donor nature of the reaction, a change in activity in the opposite sense to the change in conductivity could have been predicted (i.e., an increase in activity on irradiation). In fact, the irradiated specimen was found to be more active than the original material over the whole temperature range.

The basic cause of the effect of irradiation on activity is evidently to be found in the correlation between catalytic activity and electrical conductivity established by the electronic theory. Irradiation affects the electrical conductivity of a semiconductor, and changes in activity predictably follow the changes in conductivity as required by the electronic theory. The mechanism by which irradiation influences the electrical conductivity and the mechanism by which it influences the catalytic activity are not two independent problems, but a single problem. Because of the strict correlation between activity and conductivity, we can discount the second problem and concentrate on the first.

In this Section we have considered the case of a change in adsorption and catalytic properties resulting exclusively from a shift in electronic equilibrium brought about by irradiation. The radiation-induced defects which produce this shift do not themselves take part in the adsorption and catalytic acts. The memory associated with radiation-induced defects is retained for considerable times after irradiation is discontinued. As long as these defects persist, the electronic equilibrium remains displaced, the electrical conductivity retains a memory of the irradiation, and so also does the catalytic activity.

III. "MEMORY" ASSOCIATED WITH A DISTURBANCE OF THE ELECTRONIC EQUILIBRIUM

We shall now turn to the case where irradiation disturbs the electronic equilibrium in the semiconductor by generating non-equilibrium carriers without however giving rise to structural defects and impurities. We shall be considering, in other words, the ionising action of radiation. In particular, electromagnetic radiation such as visible and u.v. light, X-radiation, and gamma radiation shows this effect. (Note that gamma radiation can also produce structural disturbances as a secondary effect).

In these cases the semiconductor forgets the irradiation almost as soon as it is removed. This is the general rule. Noteworthy exceptions to this rule, in which the semiconductor retains a memory of the irradiation for an appreciable time even though no radiation defects have been produced, are far from uncommon. This Section is devoted to this anomalous memory, to its manifestations, and to attempts to elucidate its nature.

This memory consists in the following. If the semiconductor is irradiated with u.v. light and adsorption is measured some time after the end of the irradiation period, the dark adsorption capacity is sometimes found to be higher than before irradiation, and conversely the photoadsorption capacity is lower. The surface retains a memory of the irradiation after the irradiation has been removed, even though the production of radiation-induced defects in the sample by u.v. light is, of course, out of the question. This memory disappears very slowly, and can be completely erased only by heating the sample. A memory of this type has been observed by Solonitsyn[7] in his work on the adsorption of O_2 on ZnO.

This memory sometimes manifests itself in the kinetics of photosorption. If radiation is applied after the establishment of adsorption equilibrium, additional adsorption due to the radiation can be observed (photoadsorption). This continues by a kind of inertia for some time after the radiation is interrupted. This memory effect, which could also be termed the delayed action effect or "post-effect", has been observed by Coekelbergs and coworkers[8] during their investigation of the effect of X-radiation on the adsorption of O_2 and CO on Al_2O_3. As in the work of Solonitsyn, there is no possibility of radiation defects having been produced. Again, an increase in temperature tends

to eliminate the effect. At high enough temperatures the "post-effect" disappears completely.

Many experiments on the nature of the adsorption centres produced by irradiation and persisting on the surface for an appreciable time after the end of the irradiation period have been carried out in recent years: these experiments throw some light on the origin of this type of memory. The centres are shown to be non-equilibrium carriers generated by irradiation and captured by intrinsic defects of the surface, i.e. by defects not produced by the radiation.

Thus, the work of Kohn and Taylor[9,10] has shown that gamma irradiation of Al_2O_3 gives rise to adsorption centres for H_2 consisting of holes localised on Al atoms present in stoichiometric excess. Subsequently, Boreskov and coworkers[11] demonstrated that these centres are responsible for the catalytic activity towards the H_2–D_2 exchange reaction. Lunsdorf and Jayne[11,12] showed that u.v. irradiation of MgO produces colouration and an ESR signal due to an electron localised on an anion vacancy. Exposure to CO_2 caused bleaching of the colour and a change in the ESR signal, the new signal corresponding to the CO_2^- radical-ion. The same effect was found in the adsorption of the O_2 molecule, which was converted into the O_2^- radical-ion. Adsorption on *F*-centres produced by previous irradiation was involved also in the work of Bauer and Staude[13] on the adsorption of quinone on coloured AgBr crystals. Colourless crystals had no adsorption capacity at all. A similar effect was found by Rakityanskaya[14] in her work on the adsorption capacity of various alkali metal halide crystals before and after u.v. irradiation.

All these experiments suggest that irradiation can activate a surface by converting its natural structural defects into more or less long lived adsorption centres. Only thus can the memory exhibited by the surface in these systems be explained. We are dealing with adsorption at localised carriers which, from the standpoint of the electronic theory, play the role of localised unsaturated valencies. These centres are formed before adsorption, if irradiation is applied before adsorption, or alternatively they can be formed during the adsorption process if adsorption is taking place during irradiation. The problem of adsorption on a carrier trapped on a defect was treated quantum-mechanically by Bonch-Bruevich[15] in 1953, and later by Hauffe[16] from the point of view of the Boundary Layer Theory (Randschichttheorie), and by Kogan and Sandomirskii[17] and by one of us[1] from the standpoint of the electronic theory.

We have made a theoretical study[18] of the laws of adsorption on centres whose concentration is affected by irradiation. Ionisation followed by localisation of electrons (or holes) on defects leaves the system in a metastable state, i.e. in an excited state such that the system must overcome an activation barrier in order to pass into the stable state. It is because of this barrier that the centres created by the irradiation are relatively stable. As long as the concentration of centres remaining after irradiation has not decayed away, the surface shows an enhanced adsorption capacity. This was observed also by Solonitsyn, who exposed his specimens to preliminary irradiation. Under these conditions, however, the photoadsorption capacity can be shown to be less than before the preliminary irradiation. This is because the additional irradiation can only create a relatively small number of new centres, the bulk of the new centres having been produced during the preliminary irradiation. These phenomena have indeed been observed in practice.

At the same time, some peculiarities are observed in the kinetics of photoadsorption. If the rate of creation of adsorption centres exceeds the rate at which these centres are filled by gas molecules, the centres will continue to be filled by gas molecules even after the irradiation is stopped until an equilibrium between the surface and the gas phase is reached. Under these conditions we would expect to find a "post-effect" — the effect actually observed by Coekelbergs and coworkers but given a different interpretation in the interesting paper already quoted[8].

Having developed a theory of adsorption at a surface with a variable number of adsorption centres, we are led to the conclusion that photoadsorption is irreversible (or, more accurately, slowly reversible), that the activation energy of photoadsorption is negative, and to various other conclusions which are consistent with experimental results.

We have discussed some problems in the radiation chemistry of semiconductor surfaces. The central problem is that of the memory which the semiconductor retains after irradiation. We have considered the case of irradiation causing a shift in the electronic equilibrium, and the case of a disturbance in the electronic equilibrium. These two cases correspond, respectively, to a memory arising from radiation defects produced by the irradiation and lasting for an appreciable time and to a memory arising from the localisation of non-equilibrium carriers on structural defects, also for an appreciable time. Thus we have been concerned with two types of memory, of different origin.

The electronic mechanism of chemisorption and catalysis is particularly relevant to the influence of irradiation on the adsorption and catalytic properties of semiconductors. The electronic theory of chemisorption and catalysis is the key to an understanding of the phenomena observed during irradiation. At the same time, these phenomena are a basis for further development of the electronic theory.

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Countercurrent Fractional Crystallisation

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Countercurrent fractional crystallisation (CFC) has been attracting increasing attention in recent years. The role of CFC among other methods of separation and purification based on crystallisation is described. Various specific arrangements for applying CFC are given. Different theories of CFC are examined, and the limitations of the process are discussed. 73 references.

CONTENTS

I. Introduction 728
II. Basic principles of CFC 729
III. Types of apparatus for the separation and purification of materials by CFC 729
IV. Theories of CFC 732
V. Fields of application of the CFC method 735

I. INTRODUCTION

Effective methods of separation and purification of materials involve repeated application of the elementary processes which constitute the basis of separation. These processes are: evaporation–condensation (in the case of distillation); sorption-desorption (in chromatographic separation); evaporation–crystallisation (in fractional sublimation); fusion–crystallisation (in countercurrent fractional crystallisation), etc. Thermodynamic partition coefficients, calculated from the chemical potentials of the various phases[1], can be defined for each elementary process.

As a rule, partition coefficients for the fusion–crystallisation process are high enough to ensure efficient separation and purification of materials. These high partition coefficients are due to the fact that in most systems of practical importance the impurities form eutectics with the main component. The thermodynamic partition coefficient of a mixture of a eutectic and a pure component tends to infinity. In some systems, however, mixed crystals, peritectics, or intermediate compounds are formed. Even more complicated systems exist, particularly in multicomponent mixtures. These mixtures are characterised by a finite partition coefficient, which makes their separation more difficult. Systems of this type can be used to evaluate the effectiveness of apparatus and to determine the parameters of the separation process. Most convenient for this purpose are the two-component systems which give rise to solid solutions (just as systems giving ideal solutions are used to study fractional distillation).

The present review will examine the theory and practice of only one of the methods of separation and purification based on crystallisation: countercurrent fractional crystallisation.

The theoretical aspects of the crystallisation process have already been adequately discussed in review articles[2,3].

Modern crystallisation methods of separation and purification can be classified into a number of groups, each of which has its own advantages and disadvantages.

The most widely known of these is the zone melting method[4], which gives products of the highest purity and is generally applied in the production of ultrapure metals, semiconductors, etc. However, in spite of later refinements to increase the number of zones per pass, to provide continuous operation, and to raise the efficiency[5], the purification process remains very slow, requiring many days or at least many hours, and its production capacity is therefore low. Furthermore, the separation of large amounts (tens per cent) of impurities is problematic. The same strictures apply to the directional crystallisation method.

The fractional crystallisation method, widely used in the past, is now hardly ever used as it is extremely laborious, and has been replaced by more satisfactory methods. Somewhat improved variants of the fractional crystallisation method are the continuous methods of fractional melting[6] and partial freezing[7], which can be used in laboratory practice but are hardly likely to find industrial applications because of the low efficiency of separation which they afford.

The method called chromatographic crystallisation by Findlay and McKay[8], proposed by Bowman[9] in 1947, consists in the following procedure: a temperature gradient is applied to a column filled with a filtration medium, and the mixture to be separated is applied at the top in the solid form. The mixture is brought into the liquid form by dissolution in a solvent which does not freeze at the separation temperature (or, alternatively, by fusion). The liquid is allowed to flow downwards, simultaneously moving the temperature gradient in the

direction of the flow. The solid phase, consisting of the recrystallised mixture, is retained by the filtration medium. This process is equivalent to a countercurrent of the phases in the temperature gradient. The method gives good results only if a solvent is used. When working with a melt, as described in the original patent[9], we can expect a large amount of melt to be retained in the packing, and this can make the operation of the equipment difficult. Successful separation of paraffins has been achieved by using large volumes of solvent, but in this case the output of the apparatus falls off considerably. The method was later proposed for use in polymer fractionation[10], and is now mainly used for that purpose.

Countercurrent fractional crystallisation (CFC) has become very widely used in recent years, and has reached the stage of industrial application in many countries. The present review is devoted to this method.

II. BASIC PRINCIPLES OF CFC

Any method of separation, to be fully efficient, must meet the following requirements:

1. A multiplicity of elementary separation steps, which in principle should lead to a large number of theoretical plates.
2. Countercurrent motion of the phases, ensuring a large number of elementary steps and a distribution of the component concentrations along the length of the separating equipment.
3. Flow reversal (reflux), which leads to products of maximum purity.

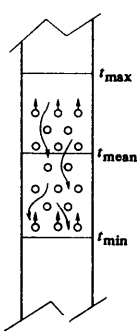

Figure 1. Schematic representation of countercurrent fractional crystallisation.

These factors also characterise the separation of materials by continuous (countercurrent) fractional crystallisation, using separating equipment working on the following principle (Fig. 1). A temperature gradient such that the maximum temperature t_{max} and the minimum temperature t_{min} are respectively higher and lower than the melting point of the mixture and of all its components and eutectics is imposed on the column. The solid phase is continuously moving with respect to the temperature field towards higher temperatures, and melts, and the liquid countercurrent flows between the crystals in the direction of lower temperatures, and freezes. Elementary fusion–crystallisation (or dissolution–crystallisation steps take place over the entire length of the separation layer, leading to a redistribution of the components between the phases. As a result, the less fusible (or less soluble) components migrate towards the hot end of the separation layer, and the more fusible components migrate towards the cold end.

It can be seen from this schematic description of the process that a fairly close analogy exists between CFC from the melt and fractional distillation: this analogy has been pointed out by a number of workers[11,12]. However, there are also a number of essential differences between the two processes. Firstly, because of diffusional limitations in the solid phase[13], the redistribution of components between the phases is achieved mainly by complete fusion of the crystals and formation of crystals of different composition. Secondly, the density difference between crystals and liquid is not usually very large, and countercurrent of the phases is usually achieved by moving one phase relative to the other by some mechanical device. Thirdly, a much greater amount of liquid is entrained in the solid phase by surface tension in its most general sense (occlusion, adsorption, capillarity). As a result, the real partition coefficient is significantly lower than the thermodynamic partition coefficient.

Due allowance for these differences must be made when the formulae and ideas used in fractional distillation are applied to the operation of crystallisation apparatus.

The profound influence of pressure on crystallisation and melting processes must also be stressed[14–16]. Excess pressure can modify the phase diagram of the system and thus affect the separation process: in this context, the application of fluctuating pressure offers the promise of new and improved types of apparatus[17–19] for the separation of materials by CFC (by varying the rates of fusion and crystallisation during each cycle of pressure change).

III. TYPES OF APPARATUS FOR THE SEPARATION AND PURIFICATION OF MATERIALS BY CFC

The equipment described in the literature can be divided into a number of groups, differing in respect of the method used to impart relative motion to the liquid and the solid phase, the extent to which the separator is filled, the method of extracting and supplying heat, and so on.

1. One variant of CFC from solution was described above under the heating "chromatographic crystallisation"[9]. In another similar variant the column is filled with solvent instead of a filtration medium[20]. The cooler is at the top of the column, the heater at the bottom, and the temperature gradient is produced by the moving streams of the phases. Countercurrent motion of crystals and solution is produced by the density difference of the phases, and is assisted by stirring the solution.

2. The use of drums for the separation and purification of materials is described in the patent literature[21,22]. The apparatus consists of a number of stages. Solid phase freezes from the melt on to the surface of the drum, which is cooled from below, and is transferred to the high-temperature region by the rotation of the drum. The drum and its associated equipment for the countercurrent transfer of crystals and melt from stage to stage can be either horizontal or sloping. A heater and a cooler are provided at each stage. The only difference in principle between this process and fractional crystallisation is the absence of filtration. The separation is not induced by a temperature gradient, but by the different rates of melting and crystallisation of the various components. The separation

efficiency is not high, because each stage contributes much less than one theoretical plate to the separation.

3. Graham's rotary crystalliser[23] is an example of the application of pressure to crystallisation processes. The partially crystallised material is passed through rollers, the lower roller being cooled and the upper being heated. The rollers squeeze the mother liquor from the crystals; also, due to the combined effect of the temperature difference on the rollers and of the pressure on the crystals, part of the crystals melts, providing additional scrubbing of the crystals. The purification efficiency is low. Even in the purification of mixtures which form a eutectic the enrichment of the desired component is only from 76 to 90%.

4. Various forms of scraping crystalliser for the separation of materials have been described[24,25]. The crystals, formed on the cold walls of the cooled end of the column, are transferred by scrapers to the hot end. However, these crystallisers have a low separation efficiency and are used only as an auxiliary means of supplying the crystalline paste to the main separating column[8].

5. The apparatus described by Carney[26] is an example of another type of crystalliser for the purification of materials. The layout is shown diagrammatically in Fig. 2: it consists of a column with a cooler *1* at the bottom and a heater *2* at the top. Countercurrent of the crystals and the melt is induced as follows: the crystals are caught in perforated compartments attached to an endless conveyor belt *3*, and move upwards, and the liquid flows under the influence of gravity. Feed material is supplied in the middle of the column (*4*), and the pure product and the near-eutectic mixture are taken off at the top (*5*) and the bottom (*6*) of the column respectively.

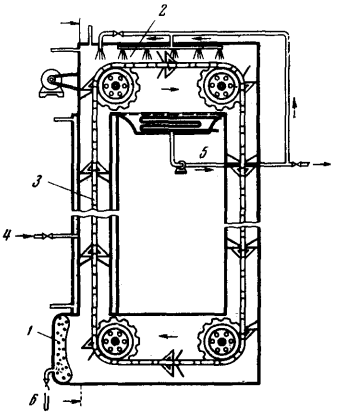

Figure 2. Carney's apparatus.

Using a reflux ratio of 9, dimethylbutane of 99% purity has been produced with a throughput of 3.1 kg h^{-1}.

6. The following types of crystalliser for the purification of materials are disclosed in a number of patents by Weedman and Findlay[27-29]. The crystalline paste is loaded into the column, which can be vertical or horizontal, or alternatively is produced directly in the column. The crystals are moved by a perforated or porous piston towards the heater: they melt, and the resulting liquid flows in the opposite direction towards the piston and filters through it. After one pass of the piston the crystalline residue is taken off as pure product. Although products (such as benzene) of up to 98–99% purity have been obtained in this apparatus, the efficiency of the apparatus must be judged unsatisfactory, since the impurities gave eutectics with the main component.

None of these types of separating equipment has found industrial application, and they are rarely used even in laboratory practice. This is due first and foremost, we believe, to their low efficiency (of the order of 1–2 theoretical plates); furthermore, they are quite complicated when fully engineered and their throughput is low.

7. The use of centrifugation for CFC was proposed by Findlay[30], but the process was first described in full detail by Fleischer[31] in 1962. Essentially, countercurrent of crystals and melt (which must have different densities) is induced in a centrifuge exposed to a temperature gradient such that the minimum temperature (sufficient to cause crystallisation) is near the axis and the maximum temperature (sufficient to cause melting) is near the periphery of the centrifuge. The crystals which have grown to a critical size (determined by the speed of rotation of the centrifuge and by the density difference between crystals and liquid) are impelled in the direction of higher temperatures by the centrifugal field, and the liquid undergoes the opposite flow towards lower temperatures. Supply of feed material and take-off of the separated components are provided on a continuous basis.

The theory of the CFC method in a centrifugal field was developed by Anikin[32] in 1963, but the first purifications[33] (by a batchwise variant) were reported in 1966. Sixteen-fold enrichment of triphenylchlorosilane was achieved in 30 min, but the separation could not be improved by longer operation. Unfortunately, the type of impurity removed is not stated, nor whether the impurity gave rise to mixed crystal or eutectic formation, and therefore the efficiency of the separation cannot be estimated.

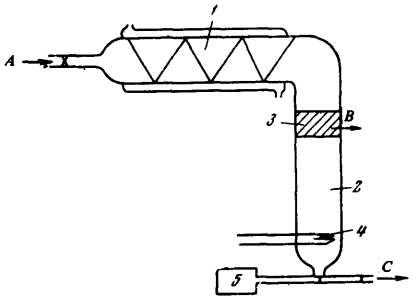

Figure 3. Diagram of the apparatus used by the Phillips company: *A*) input of feed material; *B*) take-off of mother liquor; *C*) take-off of pure product.

8. The variant proposed by Arnold[34,35] and realised by Thomas[36] has proved to be the best for use in industry. The principle of this process has been discussed by McKay and coworkers[8,37,38]. The apparatus (Fig. 3) consists of a preliminary scraping crystalliser *1*, where the crystalline paste is formed, the enrichment section *2* (corresponding to the purification column) with a porous partition *3*, heater *4*, and the pulsatory pump *5*. In a previous form of the apparatus a piston located above the porous partition

was used instead of the pulsatory unit. The piston (or pulsatory unit) operates at 90–350 cycles per minute, and alters the pressure by approximately 1–100 atm during each cycle.

The crystalline paste from the preliminary crystalliser is fed to the enrichment section of the column, the crystal content of the paste being more strictly controlled the higher the required purity of the product. During the period of pulsation corresponding to rarefaction, the paste is drawn downwards and some air is sucked through the porous filter, creating voids in the crystalline paste. During the compression period of the pulsation unit the melt is forced upwards through the crystals, and some of the mother liquor is run off through the porous filter. In the region of the heater the crystals melt: part of the melt is taken off as pure product, and part is displaced upwards by the feed crystals as a reflux. Under these conditions, both scrubbing and recrystallisation of the settling crystals occur in the region between the heater and the porous filter. In this way, a countercurrent of crystals and melt is generated in the column. The temperature gradient in the separating part of the column is generated by the flow of heat carried by the reflux from the heater to the cooler.

A later variant[39] of the same apparatus has the heater in the upper and the cooler in the lower part of the column, so that the directions of motion of the liquid and the solid phase are reversed.

The separation efficiency of the piston version of the apparatus is 3.3 theoretical plates for a column approximately 25 cm in diameter and 2.5 m long operated at a reflux ratio of 95. The capacity of these installations for the separation of eutectic-forming impurities is extremely high. An industrial column operated by the Phillips Company, with pulsation unit, has an output of 60 000 metric tons of *p*-xylene per annum.

9. There is a very large group of assemblies[40–43] in which the countercurrent flow of crystals and melt (or solution) is obtained by moving the crystals from the cooler to the heater by means of a worm-screw or spiral. The melt formed in the vicinity of the heater is displaced by the flow of crystals or flows under the influence of gravity towards the cooler. The most efficient assemblies of this kind are the laboratory crystallisation columns for batchwise or continuous operation developed by Schildknecht and coworkers[44–47].

An apparatus of this type is shown diagrammatically in Fig. 4. It consists of a glass column R_1 with a graded heater winding W and a spiral S, which rotates between the inner (R_2) and the outer tube, impelling the crystals downwards in the temperature gradient (i.e. towards the hotter part of the column). Liquid is displaced upwards by the crystals. Assemblies of this type have been tested for the purification of many organic compounds such as phenanthrene, benzene, cyclohexane, biphenyl, fluorene, azobenzene, β-naphthol, etc. Columns of this type have been used also for the separation of inorganic salts[48]. The results indicate a high operating efficiency, but the data quoted in different papers are somewhat contradictory. Schildknecht et al.[49] published a graph of the melting point of fractions at different heights in the crystallisation column for the purification of phenanthrene. Most of the material (the purer fractions) had a melting point of about 110°C, but after three zone-melting passes the melting point of the purer fractions was raised to 210°C. †

† Although the increase in melting point achieved seems surprising, these data are in fact more or less consistent with the claims advanced in the original paper (Ed. of Translation).

Schildknecht and Vetter[50] have compared the results of the purification of hexadecanol by zone melting and column crystallisation methods. The highest melting point after zone melting (20 passes, velocity of the zone 1 mm h^{-1}) was ~ 50°, and after 2.5 h column crystallisation the melting point was ~ 53°. In both cases, the main bulk of the material had a melting point of ~ 49.5°. Thus, in the purification of phenanthrene the purest product was obtained by zone melting, whereas column crystallisation gave the purest hexadecanol.

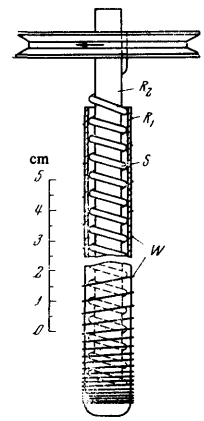

Figure 4. Schildknecht's apparatus.

There are some discrepancies between the published estimates of the efficiency of this method. Thus, Ammon[48] quotes an efficiency of up to 5 theoretical plates for a column length of 25 cm. Schildknecht[51], referring to Rössler's thesis[52], obtained an efficiency of 8–10 theoretical plates in a 20 cm column, corresponding to a value of 2–2.5 cm for the height equivalent to the theoretical plate (HETP). Powers[53] measured the efficiency in terms of the number of unit transfers (NUT) and height for unit transfer (HUT). Using the same data from Rössler, the HUT was 3.3 cm for the azobenzene–stilbene system, which forms mixed crystals, and 12.3 cm for systems giving rise to eutectics. Since the details of Rössler's work are not available in the literature, it is not profitable to discuss the origin of these discrepancies.

To achieve comparable purification (i.e. similar concentration distributions along the column), zone melting requires ~ 10 days as compared with ~ 2.5 h for column crystallisation. The output of crystallisation columns 1–2 cm in diameter and 15–20 cm long is 8–10 g h^{-1}, which makes them fully acceptable for laboratory purposes in spite of some constructional difficulties.

10. The following variant of CFC was proposed[54] in 1964. Column *1* (Fig. 5), with a layer of crystals frozen on its walls to a thickness of not more than 1–2 mm, is moved with respect to the heat exchanger *4*, designed to give a temperature gradient sufficient to keep the upper part of the column above (and the lower part of the column below) the melting points of all the components and eutectics of the mixture to be separated. The liquid flows by countercurrent between the crystals towards the lower-temperature regions under the influence of gravity. Fusion

and recrystallisation processes take place over the entire length of the layer to be separated, and as a result a gradient of component concentrations arises along the column. This process differs from those already described in the following respects: separation takes place in a thin (0.1–0.2 mm) layer which is moving with respect to the heat-conducting column wall, and the heat exchanger imposes a forced temperature gradient (independent of the mixture to be separated). These two special features offer the following advantages: (1) much faster supply of heat to the crystals and removal of heat from the liquid, accompanied by a higher rate of mass exchange, since heat exchange between the phases can occur by heat transfer through the wall as well as by direct contact between the phases; (2) formation of the main bulk of the crystals directly on a heat-conducting surface, which minimises the entrainment or partially melted crystals by more fusible material; (3) the fusion and crystallisation processes and the temperature gradient are practically independent of the mixture to be separated, leading to minimal retention of material by the separation apparatus: in the batchwise variant of the method separation of a mixture into its primary components can be achieved without appreciable formation of intermediate fractions; (4) stable operation of the apparatus, since the liquid moving towards temperatures below the melting point and the crystals moving towards temperatures above the melting point are subjected to ever-increasing temperature differences which tend to arrest their motion; (5) temperature uniformity over the cross-section of the layer to be separated.

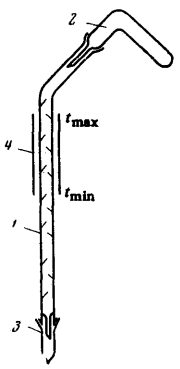

Figure 5. Thin-layer CFC apparatus.

Because of these advantages, the separation apparatus has a very high efficiency. The number of theoretical plates and the number of unit transfers, measured with a standard benzene–thiophen mixture giving mixed crystals [55], are practically equal, and can be as high as 25–30 in the most favourable cases. The HUT and HETP are 2–2.5 cm. The maximum purity of the product (in the absence of eutectic-forming impurities) was 99.9995%. The output of the batchwise laboratory variant of the apparatus is about 10 g h^{-1}. With the continuous variant the output should be at least 1–2 kg h^{-1} from a meter of column perimeter.

The way in which the temperature gradient is moved with respect to the layer to be separated has been shown to be immaterial. It is possible to move the column, the heat exchanger, or even the temperature gradient directly (for example, by passing through the heat exchanger a liquid whose temperature is increased according to a predetermined programme).

Thin-layer operation of CFC is discussed in a number of American papers published in 1965. However, the construction of the apparatus [56,57] is described sketchily, and nothing is said about process parameters or about the operating efficiency of the equipment. The only statement is that the purity of the product can be as high as 99.999–99.9999%.

The high efficiency (8–10 theoretical plates) achieved in devices of the Schildknecht type is probably due to the fact that they operate under conditions approximating to those obtaining in thin-layer separation.

IV. THEORIES OF CFC

A single theory encompassing all methods of CFC is not available at present. Hence, different variants of the theory must be considered, each of which is applicable only to a particular method of separation. The only feature which is common to all these variants is that the CFC process is treated by analogy with fractional distillation, with large or small departures. As in fractional distillation, the efficiency of the separation apparatus is discussed in terms of HETP and N (the height and number of theoretical plates) or of HUT and NUT, of the throughput, and of mass and heat balance.

However, whereas in fractional distillation the partition coefficients are always finite, the thermodynamic partition coefficient for crystallisation with eutectic formation is infinite, and in principle complete separation into one component and the eutectic should be possible with an efficiency of a single theoretical plate. In this case two approaches can be used to calculate the efficiency of separation. In the first the degree of enrichment (and therefore the extent of the approximation to a theoretical plate) is calculated. The second approach requires allowance for the real composition of the phases: the composition of the liquid phase is assumed to remain unchanged, but the composition of the crystalline phase is calculated with allowance (by various means) for the liquid which wets the crystals. Both approaches are found in the literature, and we shall mention them again in the discussion of the various theories. The principles of the calculations for some of the methods described in Sections III.1–III.10 will now be briefly reviewed.

Section III.1 describes a column in which the motion of the crystalline phase in the solvent is caused by density differences. Ciolan [58] has calculated the dependence of the yield on the enthalpies and specific heats of the components starting from the mass and heat balance equations for the enrichment and the exhaustion sections of the column.

Section III.7 describes the operating principle of crystallisation columns in a centrifugal field. The theory developed by Anikin [32] for this system assumes the fullest analogy between CFC and fractional distillation, with the hypothesis that diffusion is fast enough in a solid in a "state of pre-fusion" to produce concentration uniformity in the crystalline phase. The expressions for the time needed to reach steady state and for the ratio of the ultimate concentrations are the same as those obtained by

Cohen[59] for fractional distillation. The fluxes are calculated by combining the centrifugal field and the rate of growth of the crystals.

Devyatykh[60] holds similar views on the overriding role of diffusion in the solid phase during the separation process. By considering the material balance in the column and assuming a steady state he arrives at the following expression for the efficiency under total reflux:

$$\mathrm{HETP} = \omega^2/3D_1\kappa,$$

where L is the flux of solid phase, 2ω is the mean thickness of the platelets of crystalline phase, D_1 is the diffusion coefficient of the minority component in the solid phase, and κ is the fraction of the volume of the column occupied by the solid phase.

It should be noted that most workers consider diffusion in crystals in a state of pre-fusion to be abnormally high but nevertheless 1–2 orders of magnitude lower than in the liquid[13,61]. Using a stage-by-stage treatment of the crystallisation process, Anikin[62] obtained an expression for the number of theoretical plates also analogous to the equations used in distillation and zone melting.

In Section III.8 we have mentioned the efficient separation achieved by the piston column used by the Phillips Company on a pilot-plant scale. The efficiency was determined for the separation of a mixture of cyclohexane and methylcyclopentane, whose phase diagram is quite complicated but can be interpreted as mixed crystal formation in the concentration region between 50 and 100% of cyclohexane. The HETP is 75 cm. Subsequent refinements, including replacement of the piston by a pulsation unit, more precise control of the operating conditions[63,64], on-line computer control[65,66], etc. must obviously have increased the separation efficiency somewhat, but the Phillips columns are still used exclusively for the separation of eutectic-forming impurities. We note that in this case a single theoretical plate is sufficient in principle. Hence, the main interest is not in calculations of efficiency but in the column fluxes and throughputs.

The influence of a number of variables on the purity of the product and on the yield of the column has been discussed[37,38]. Factors such as the crystal content of the paste, the viscosity of the mother liquor, the size of the crystals, the pulsation frequency, etc. have been shown to play an important part. However, the basic factors which determine the operation of the column are: the reverse flow of liquid (reflux), the heat balance, and the degree of recrystallisation in the purification zone. In the words of the authors, recrystallisation is "the key to purification in the column". The degree of recrystallisation can be calculated by carrying out a mass and heat balance for the purification section, making the following assumptions for any cross-section of the column: the occluded liquid is in equilibrium with the crystals; the free liquid rising in the column is at the freezing point and its composition is given by the phase diagram for the system; the ratio of the amounts of solid phase and of occluded liquid is constant; the flow of heat through the column wall is zero.

With these assumptions, the mass and heat balance equations take the form

$$S = W + L - O;$$

$$\Delta H = H_L L - H_O O - H_S S + K(t_L - t_S);$$

$$O = \frac{(1-X_L)[H_S W + \Delta H - K(t_L - t_S) + W(1-X_W)(H_L - H_S)]}{(1-X_O)(H_L - H_S) - (1-X_L)(H_O - H_S)},$$

$$L = \frac{O(1-X_O) - W(1-X_W)}{1-X_L},$$

where S is the flux of solid phase, W is the flux of product, L is the flux of rising liquid, O is the flux of occluded liquid, H is the enthalpy, ΔH is the nett flow of heat in the column, t are temperatures, K is a parameter (including the thermal conductivity of the solid phase, the cross-sectional area of the column, the constant temperature difference between the rising liquid and the falling crystals, and the rate of change of temperature per unit height of the layer), and X is the concentration of the desired component. If the concentration of the crystalline paste entering the column is also known, the degree of recrystallisation can be calculated as the ratio of the amount of newly formed crystals to the amount of crystals entering the column.

McKay and Goard[67] give the following formula for the degree of recrystallisation in the piston column:

$$R = \frac{(T_p - T_c)C_p}{H_f},$$

where R is the degree of recrystallisation, T_p and T_c are the melting points of the pure crystals and of the crystals entering the purification zone, C_p is the mean specific heat of the crystals in the temperature range between T_p and T_c, and H_f is the heat of fusion of the purest component.

In the purification of p-xylene the optimum degree of recrystallisation was ~ 0.2–0.3, and the throughput of the column was as high as 3.23 $m^3\ h^{-1}$ for a cross-sectional area of 1 m^2. It should be noted that the reflux ratio of the liquid must be raised very considerably (to 95 : 1) when the impurities form mixed crystals with the main component: under these conditions the throughput of the column decreases sharply.

A crystallisation column in which the crystalline phase moves with the help of a rotating spiral is described in Section III.9. The CFC variants proposed by Schildknecht and coworkers have been discussed theoretically by Powers[53]. When the system contains mixed crystals, the author makes the following assumptions: phase equilibria are not reached; diffusion in the solid phase is negligibly small; the flux of crystals is constant along the length of the column. Under these conditions the rate of transfer of component A from one phase to the other is defined by the expression

$$\zeta_A = y_A L - x_A C - \rho D A \Phi \frac{dy_A}{dZ}.$$

For equilibrium within an element dZ at a height Z in the column the expression for the rate of transfer takes the form

$$\frac{d(x_A C)}{dZ} = K_t a A (y_A^* - y_A),$$

where x_A is the concentration of component A in the solid phase, y_A is the concentration of A in the liquid, L and C are the fluxes of liquid and of crystals, ρ is the density of the liquid phase, D is the diffusion coefficient in the liquid, A is the total area of the column cross-section, Φ is the volume fraction of the liquid phase, a is the contact area of the phases per unit volume of the column, and K_t is the mass transfer coefficient.

At steady state we can write

$$L = C; \qquad \frac{dX_A}{dZ} = \frac{dy_A}{dZ}.$$

In this case we obtain the following expression for the nett rate of transfer under total reflux:

$$\tau_A = C(y_A^* - x_A) - \left[\frac{C^2}{K_t a A} + \rho D A \Phi\right]\frac{dx_A}{dZ}.$$

Noting that at equilibrium $\tau_A = 0$, and assuming that all factors in square brackets are independent of Z, we can write the equation in an integral form:

$$\frac{Z}{\left[\frac{C}{K_t a A}+\frac{\rho DA\Phi}{C}\right]}=\int_{x_A(0)}^{x_A(Z)}\frac{dx_A}{y_A^*-x_A}\ .$$

The denominator of the left-hand side of this equation contains all the parameters of the column referred to unit length: it may be termed the height for a unit transfer (HUT). The value of the integral depends only on the final compositions and on the equilibrium equation $y_A^* = f(x_A)$. It is a direct measure of the difficulty of separation, and is usually expressed as the number of unit transfers (NUT).

Given the indeterminate but fixed lower limit of the integration, it is possible to evaluate the integral as a function of x_A for any system from the phase diagram. We note that for $x_A = 0$ or $x_A = 1$ the integral tends to infinity. Hence, Powers considers complete separation theoretically impossible. Once the distribution of the concentration x_A along the column is known, the integral can be evaluated as a function of the length Z.

The slope of this linear equation, given by

$$m=\frac{1}{\left[\frac{C}{K_t a A}+\frac{\rho DA\Phi}{C}\right]}=\frac{1}{\mathrm{HUT}}\ ,$$

defines the HUT. The NUT can be calculated from the formula NUT = Z/HUT. Experimental results actually give straight plots, showing that all factors in square brackets are indeed independent of Z.

In his discussion of eutectic systems Powers makes the following assumptions: the system component A–component B is treated as a binary component A–eutectic system in which the eutectic plays the part of a new component B_1; the liquid containing the impurity is in contact with pure crystals of composition A everywhere along the layer to be purified except at the upper end, where the composition of the crystals changes discontinuously to the eutectic composition.

Let the crystals be the pure component A ($x_E = 0$), and let the liquid in contact with them have the composition y'_E and velocity L', in contrast to the composition y_E and velocity L of the main bulk of the liquid. But for these special features, the subsequent discussion is in no way different from the case of mixed crystals. The rate of mass transfer between the adherent liquid and the rising liquid is proportional to the concentration difference:

$$W_E = K_t a (y'_E - y_E)\ .$$

Introducing the balance equations, we arrive at the following expression for the transfer in the total reflux region:

$$\tau_E = Cy'_E - \left[\frac{L'(L'+C)}{K_t a A}+\rho DA\Phi\right]\frac{dy'_E}{dZ}\ .$$

At steady state $\tau_E = 0$, and the integral form is

$$\frac{y'_E}{y'_E(L)}=\exp\left[\frac{C(Z-L)}{\frac{L'(L'+C)}{CK_t a A}+\frac{\rho DA\Phi}{C}}\right]\ ,$$

where $y'_E(L)$ is the concentration of the adherent liquid at the top of the column, L is the total length of the column, and y'_E is the concentration of the adherent liquid at the point Z. When using this expression, we must remember that the model changes as soon as the liquid reaches the eutectic composition. Under these conditions the crystals, the adherent liquid, and the rising liquid all have the eutectic composition.

To test the application of this equation to experimental data, a linear variation of composition with temperature was assumed. In this case we have

$$\frac{y'_E}{y'_E(L)}=\frac{T_B-T(Z)}{T_B-T(L)}\ ,$$

where T_B is the melting point of the pure component, $T(Z)$ is the temperature at point Z, and $T(L)$ is the temperature at the upper end of the column. As stated above, when Rössler's experimental results are examined in the light of this theory, large differences are found between the heights for unit transfer in the case of systems forming mixed crystals or eutectics (3.3 and 12.3 cm respectively).

The separation process described in Section III.10 for binary mixtures forming mixed crystals has been discussed[68] by making the following assumptions: steady state is not achieved; fusion of the crystals is not accompanied by change in composition, because diffusion in the solid phase can be ignored; a change in composition occurs when the liquid crystallises, the composition of the resulting crystals being determined by the liquidus curve.

Hence, using the expressions for material balance and for the rate of transfer of a component from one phase to the other, the following expression was obtained for a given instant:

$$\int_0^Z \pi D\frac{\delta_l \bar{l}}{S}dZ=\int_{y_0}^{y}\frac{dy}{x^*-y}$$

where Z is the length of the layer, δl is the effective thickness of the liquid, $\bar{l}$ is the rate of melting (mole cm^{-3} h^{-1}), S is the flux of solid phase, y and x are the concentrations of one of the components in the crystals and in the liquid, x^* is the concentration of the same component in crystals in equilibrium with x. As was shown from experimental data, replacing y by $\bar{x}$ (where $\bar{x}$ is the mean of the concentrations x and y) and x^* by $\bar{x}^*$ does not introduce significant errors. The integral thus obtained,

$$\int_{\bar{x}_0}^{\bar{x}}\frac{d\bar{x}}{\bar{x}^*-\bar{x}}$$

can be taken as the NUT to a first approximation. The values of HUT and NUT calculated by this method are close to the HETP and N values respectively, calculated from the final concentrations by the Fenske–Underwood formula[69].

Equations have been obtained[68] relating the efficiency of operation of the separating equipment to the following process parameters: h (the length of advance of the column with respect to the temperature gradient), between 12 and 120 cm; v (the rate of advance), between 6 and 480 cm h^{-1}; m (the loading), between 0.5 and 5.3 ml per cm of column periphery. The equations are of the form

$$\mathrm{HUT} = 12\,h^{-0.44}v^{0.2}m^{0.5}\ ,$$

$$\mathrm{NUT} = 1.5 + 3.9\,h^{0.44}v^{-0.2}m^{-0.2} - 0.2\,h^{-0.56}v^{0.8}m^{-0.5}\ .$$

The variation of the separation efficiency with composition of the initial mixture and with temperature gradient has also been determined. All these expressions were obtained from experiments with a standard benzene–thiophen mixture, which gives mixed crystals.

The expression obtained above,

$$\mathrm{NUT}=\int_{y_0}^{y}\frac{dy}{x^*-y}\approx\int_{\bar{x}_0}^{\bar{x}}\frac{d\bar{x}}{\bar{x}^*-\bar{x}}$$

is not accurate enough, because it was derived without

allowance for the wetting (in its most general sense, including occlusion, adsorption, and capillarity) of the crystals by liquids of different composition. Chikin and coworkers[70] have obtained an equation which allows for wetting. If the wetting is not a sensitive function of the height (i.e. composition) of the layer to be separated, the equation has the form

$$\mathrm{NUT}_E = \frac{1}{1-C}\int_{\bar{x}_0}^{\bar{x}} \frac{d\bar{x}}{\bar{x}^* - \bar{x}} \quad ,$$

where C is the wetting coefficient, expressed as the ratio of the mole fraction of the wetting liquid to the sum of the mole fractions of the wetting liquid and of the crystals. At low values of C, corrections for the wettability have a minor effect on the calculated separation efficiencies in systems which form mixed crystals.

In the theoretical discussion of systems giving rise to eutectics the following assumptions have been made: the system consists of two components (the eutectic and one of the pure components); the composition of the liquid along the height of the column (i.e. along the temperature gradient) is determined by the liquidus curve, whereas the composition of the solid is determined by the wettability (in its widest sense) of the crystals of the pure component by a liquid whose composition is determined by the equilibrium curve. For this system, the last formula takes the form

$$\mathrm{NUT}_E = \frac{Z}{\mathrm{HUT}_E} = \frac{1}{1-C}\int_{\bar{x}_0}^{x} \frac{d\bar{x}}{-\bar{x}} = \frac{1}{1-C}\ln\bar{x}\Big|_{\bar{x}}^{\bar{x}_0} \quad ,$$

where Z is the total length of the layer to be separated. Efficiencies calculated by this formula agree almost exactly (except for the region of concentrations close to the eutectic) with the results obtained under the same conditions for the separation of materials forming mixed crystals.

V. FIELD OF APPLICATION OF THE CFC METHOD

Countercurrent fractional crystallisation is most successfully used with materials whose composition changes at their boiling point (by decomposition, polymerisation, etc.). Compounds such as methylvinylpyrrolidone and styrene[71] have been successfully purified; juices, tea, and beer[72] have been concentrated, etc. In some cases the method is economical also for the purification of materials such as *p*-xylene, naphthalene[72], etc. In all these applications the impurities formed eutectics with the main component, and therefore only moderate efficiency (but a high throughput) was required of the separation equipment. Apparatus of this type includes the Phillips columns and also the continuous variant of the centrifugal column.

For laboratory use, and for the preparation of specially costly materials in a high state of purity (drugs, some monomers, etc.), columns of the Schildknecht type or the thin-layer variant of CFC are the most suitable. These types of equipment when operated at a moderate output (tens of grammes per hour) offer extremely high separation efficiencies. The thin-layer variant is simpler to construct and offers somewhat greater efficiency.

In addition to the preparation of super-pure materials, these variants of the separation equipment can be used for the concentration of impurities, for the direct determination of eutectic compositions, etc. Apparatus for the analysis of mixtures can be designed on the basis of these assemblies.

The limitations of the CFC method must be mentioned. Separation is impossible when the composition of materials changes at the melting point or when they are very viscous at the melting point. In these cases a third substance can be added to lower the melting point or the viscosity, but this expedient lowers the output and complicates the separation.

However, in spite of these limitations, the CFC method deserves, on the whole, extensive application both in industry and in the laboratory.

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Isotopic Exchange of Hydrogen in Aromatic Complexes of the Transition Metals

V.N.Setkina and D.N.Kursanov

This paper examines and evaluates the data on the isotopic exchange of hydrogen in aromatic complexes of the transition metals. Results of the kinetic investigation of isotopic exchange of a series of metallocenes in acid media are given, and these data are compared with those on hydrogen exchange of benzenoid compounds, permitting the relative reactivity of the sandwich compounds in electrophilic hydrogen exchange to be characterised. The isotopic exchange reactions of hydrogen are used to obtain quantitative data on the influence of electron-donating and electron-withdrawing substituents on the ferrocene system. A deep difference in the nature of the interaction of the substituents with the electron systems of ferrocene and benzene has been established.

The isotopic exchange of hydrogen in alkaline media is used to evaluate the acidic properties of aromatic complexes of the transition metals and as a characteristic of the effect of the nature of the central metal atom on the reactivity of the aromatic ligands.

A combination of hydrogen isotopic exchange and proton magnetic resonance enables the partial rate of exchange of hydrogen atoms at different ligand positions to be determined and hence the quantitative evaluation of their relative reactivity. A levelling of differences in the field of the orientating action of substituents in aromatic ligands π-bonded with the atoms of the transition metals has been established.

There is a bibliography of 87 references.

CONTENTS

Introduction 737

1. Isotopic exchange of the hydrogen of ferrocene with acids 738
2. Influence of substituents on the isotopic exchange of hydrogen of ferrocene derivatives with acids 739
3. Influence of substituents on the reactivity of the 2-, 3-, and 1'-positions of cyclopentadienyl rings of ferrocene in exchange with acids 739
4. Mechanism of electrophilic isotopic exchange of hydrogen in the ferrocene series 740
5. Isotopic exchange of the hydrogen of metallocenes 742
6. Isotopic exchange of hydrogen in the aromatic rings of arenechromiumtricarbonyls 744
7. Isotopic exchange of hydrogen in cyclobutadieneirontricarbonyl 746

INTRODUCTION

With the discovery of ferrocene[1] the chemistry of the complexes of the transition metals with organic ligands underwent considerable development. It has now become a large branch of organic chemistry containing enormous factual material and of great theoretical and practical interest[2-9].

The present paper considers the results obtained in the investigation of aromatic complexes of the transition metals by the hydrogen isotopic exchange method.

A series of features of the isotopic exchange of hydrogen allows it to be considered as worthy of separate consideration. Reactions which include the replacement of hydrogen by other atoms or groups, are widely distributed in organic chemistry. Hence the isotopic exchange of hydrogen models this extremely typical and important group of reactions of organic substances. Moreover, an important feature of isotopic exchange reactions is that during the isotopic substitution the electronic structure of the molecule does not change and this allows a more general characteristic of the reactivity of a substance to be obtained than on the basis of the replacement of hydrogen by other atoms or groups.

An investigation of the kinetic isotopic effects due to a difference in the zero-point energies of molecules with C–H, C–D, and C–T bonds, frequently permits significant conclusions about reaction mechanism to be drawn, particularly about the nature of the slowest stage.

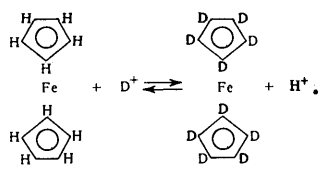
The isotopic exchange of hydrogen is sensitive to the change in the acidity of the medium. Knowledge of this dependence enables the reactivity of substances which differ considerably in their behaviour towards the acidity of the medium to be compared.

A comparison of the methods of proton magnetic resonance and hydrogen exchange allows the partial rates of exchange of various hydrogen atoms in the organic ligands to be determined and hence their relative reactivities to be evaluated quantitatively.

1. ISOTOPIC EXCHANGE OF THE HYDROGEN OF FERROCENE WITH ACIDS

The ability of the hydrogen atoms of aromatic ligands of sandwich compounds to undergo isotopic exchange with acids was first observed with ferrocene[10–12].

Nesmeyanov and coworkers[10] found that all the hydrogen atoms of the cyclopentadiene rings of ferrocene undergo isotopic exchange with acids enriched in deuterium. For example, this reaction occurs with hydrochloric, phosphoric, trichloroacetic, and trifluoroacetic acids enriched in deuterium[10,11]:



Simultaneously with these investigations a reference appeared in the literature[12] to unpublished work by Santer, who observed hydrogen exchange between ferrocene and the complex of boron fluoride and deuterium oxide.

Ferrocene reacts with concentrated deuteriosulphuric acid in a peculiar manner[11]. It was found that in this instance rapid deuterioexchange is accompanied by the oxidation of ferrocene to the ferricinium cation, which, however, is incapable of undergoing isotopic exchange. Both the competing reactions—deuterioexchange and oxidation—take place at different rates, the rate of isotopic exchange the greater, in consequence of which the oxidised form (ferricinium ion) contains a considerable amount of deuterium[11].

Quite recently Pavlik and Šubrt[13] reported that very rapid deuteriation of the cyclopentadienyl rings of ferrocene takes place during its reaction with deuterium chloride in the presence of aluminium chloride.

It was found[14] that the rate of isotopic exchange of the hydrogen of ferrocene depends significantly on the acidity of the medium. There is a linear dependence of the logarithm of the rate constant of the hydrogen exchange $k_{h.e.}$ on a function of the acidity of the medium, that is, Hammett's relation[15]

$$\lg k_{h.e.} + H_0 = \text{const},$$

is observed in the hydrogen exchange of ferrocene with acids.

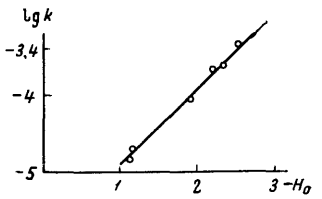


Figure 1. Effect of the acidity of the medium on the rate of isotopic exchange of the hydrogen of ferrocene.

Fig. 1 shows the results[14] which characterise the variation of the hydrogen exchange rate of ferrocene with the acidity of the solutions of trifluoroacetic acid of various concentrations in acetic acid. These results show that for ferrocene, as also for benzene[16], the rate of hydrogen exchange is proportional to the acidity of the medium.

The electrophilic isotopic exchange of hydrogen was used to study the relative reactivity of the compounds of the ferrocene series and other sandwich compounds of the transition metals. Compounds of the benzene series, whose reactivity in reactions with isotopic exchange of hydrogen has been well studied, were used as standards of comparison[17].

A comparison of the kinetic data on the hydrogen isotopic exchange of ferrocene and benzene allowed the relative reactivity of ferrocene to be evaluated. It was found that the relative rate constant for the hydrogen exchange of ferrocene ($k_{rel} = 7.8 \times 10^5$) is almost six orders of magnitude greater than that for benzene[11]. At acidities of the medium differing by six orders of magnitude the rates of hydrogen exchange of benzene and ferrocene are approximately the same.

Later Rosenblum and coworkers[18] compared the rates of acetylation of ferrocene and benzene by a Friedel–Crafts reaction and found that the acetylation of ferrocene ($k_{rel} = 3.3 \times 10^6$) is more rapid by approximately six orders of magnitude.

Hence results on the acetylation of ferrocene and benzene agree well with data on the isotopic exchange of hydrogen and show that in the electrophilic substitutions ferrocene exhibits considerably greater reactivity than benzene.

2. INFLUENCE OF SUBSTITUENTS ON THE ISOTOPIC EXCHANGE OF HYDROGEN OF FERROCENE DERIVATIVES WITH ACIDS

Before the use of the method of isotopic exchange of hydrogen quantitative information on the influence of substituents on electrophilic substitution in the ferrocene series was scarce and related only to alkyl[19], phenyl[20], and acetyl[21] groups. Quantitative data on the effect of substituents of electron-donating and electron-withdrawing character on the ferrocene system were obtained with the aid of the isotopic exchange of hydrogen with acids[22]. With this aim the kinetics of isotopic exchange of hydrogen in acid medium was studied for various monosubstituted and heteroannular disubstituted ferrocenes and the overall rate constants for the isotopic exchange of the hydrogen of these compounds were determined.

If the rate constant for the hydrogen exchange of ferrocene is taken as unity, then the relative rate constants for the exchange of substituted ferrocenes is expressed by $k_{rel} = k_{fc-X}/k_{fc-H}$. Table 1 gives the relative constants for the rate of hydrogen exchange which have been found experimentally.

Table 1. Relative constants k_{rel} of the rate of isotopic exchange of the hydrogen of substituted ferrocenes.

Substituent X	Compound	
	$C_5H_5FeC_5H_4X$	$(C_5H_4X)_2Fe$
—H	1	1
—CH_3	10.7	—
—C_2H_5	10.7	50.8
—OCH_3	6.7	23.3
—C_6H_5	0.6	0.3
—Cl	$2.5 \cdot 10^{-2}$	$7 \cdot 10^{-4}$
—$COOCH_3$	$1 \cdot 10^{-3}$	—

These kinetic results on the influence of substituents on the reactivity of ferrocene derivatives showed[23] that the logarithms of the relative rate constants of the isotopic exchange of hydrogen of the monosubstituted and disubstituted ferrocenes depend linearly on the substituent constants σ_p^0 and that the correlation coefficient r has a high value ($r = 0.992$) (Fig. 2).

Hence the substituent constants σ_p^0 determined from the dissociation constants of phenylacetic acids are a quantitative characteristic of the influence of the substituent on the rate of hydrogen exchange of the ferrocene system. These substituent constants take into account the conjugation of the substituent with the aromatic system but not the conjugation of the substituent with the reaction centre.

From the linear relation between $\lg k_{rel}$ and σ_p^0 it follows that the relation between the inductive effect and the effect of conjugation of the substituent in the electrophilic hydrogen exchange of ferrocene derivatives is approximately the same as in reactions in the side chain of benzene derivatives, that is, the contribution of the conjugation of the substituent is considerably less for the ferrocene compounds than in electrophilic substitution in the benzene series.

This conclusion follows especially clearly from a comparison of the influence of the CH_3– and CH_3O-groups on the ferrocene and benzene systems.

The methyl group, exhibiting a positive inductive effect and a positive conjugation effect (+I, +C effects), increases the rate of hydrogen exchange in cyclopentadienyl rings of ferrocene to a less extent than in benzene[24]:

$$k_{C_6H_5CH_3}/k_{C_6H_6} \simeq 150;$$

$$k_{fe-CH_3}/k_{fe-H} \simeq 10.$$

The methoxy-group, exhibiting a positive conjugation effect and a negative inductive effect (+C, –I) increases the rate of hydrogen exchange in the benzene system 40 000 times[25] but in the ferrocene system by no more than 7 times, that is, the activating influence of the CH_3O group on the benzene ring and on the ferrocene ring differ by almost four orders of magnitude.

$$k_{C_6H_5OCH_3}/k_{C_6H_6} \simeq 4 \times 10^4;$$

$$k_{fe-OCH_3}/k_{fe-H} \simeq 7.$$

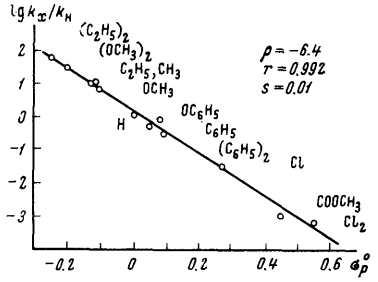


Figure 2. Variation of $\lg k_{rel}$ of hydrogen exchange on σ_p^0.

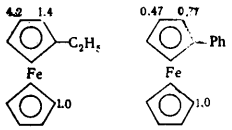
It is significant that the effect of substituents in the ferrocene series on the rate of isotopic exchange of hydrogen seemed identical with the effect of the substituents on the value of the redox potentials of the substituted ferrocenes. A linear relation was found between the logarithms of the equilibrium constants of the redox reactions and σ_p^0 by Nesmeyanov and coworkers[26] for a large number of substituted ferrocenes.

The same type of substituent effect in substitutions (isotopic exchange) and in the oxidation of ferrocene can evidently be explained by the presence in both reactions of a common reaction centre, which it is natural to assume is the iron atom.

3. INFLUENCE OF SUBSTITUENTS ON THE REACTIVITY OF THE 2-, 3-, AND 1′-POSITIONS OF CYCLOPENTADIENYL RINGS OF FERROCENE IN EXCHANGE WITH ACIDS

Quantitative information on substituent effects on the reactivity of the different positions in the cyclopentadienyl rings of monosubstituted ferrocenes is extremely scanty and, as already mentioned, is limited to data characterising the influence of alkyl, phenyl, and acetyl groups[19-21]. From these results it follows that the reaction capability of various positions in cyclopentadienyl rings (2-, 3-, and 1′-positions) is not very different for alkyl- and aryl-substituted ferrocenes. As an example, we give numerical

data on the relative reactivity of the 2-, 3-, and 1'-positions in ethyl- and phenyl-ferrocenes during acetylation[19,20].

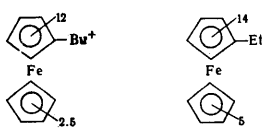


It should be noted that the determination of the reactivity of different positions of the ferrocene substituents in electrophilic substitutions involves great experimental difficulties and in several instances is impossible. For example, the influence of methoxy- and methylthio-groups on the reactivity of the ferrocene system in a Friedel–Crafts acetylation, since methoxy- and methylthio-ferrocenes seemed unstable under these conditions[27].

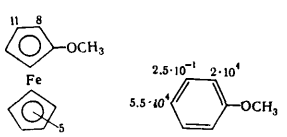
An extremely promising method of studying the reactivity of various positions in the cyclopentadienyl rings of substituted ferrocenes is evidently the method of isotopic exchange of hydrogen in conjunction with the high-resolution proton magnetic resonance (PMR) method.

The proton magnetic resonance spectra of a large number of monosubstituted ferrocenes[28] show that the differences in the chemical shifts of the signals of the protons of the 2-, 3-, and 1'-positions are rather great and consequently the deuterium content in these positions can be determined from the change in the integral intensity of the corresponding PMR signals in the isotopic exchange of hydrogen. Even for alkyl substituents, for which the differences in the chemical shifts of the corresponding protons are relatively small, success was achieved on a spectrometer with working frequency 60 MHz in separating the protons of substituted and unsubstituted rings and hence of evaluating their reactivity[29].

The values determined by this method of partial rate factors for isotopic exchange of the hydrogen of unsubstituted and substituted rings of t-butyl- and ethyl-ferrocenes with deuteriated trifluoroacetic acid have been given by Setkina[30].



The partial rate factors for electrophilic hydrogen exchange with deuteriated trifluoroacetic acid were determined in an analogous manner for the 2-, 3-, and 1'-positions in methoxyferrocene[31]. These values were 8, 11, and 5 for the 2-, 3-, and 1'-positions respectively. It is interesting that the partial rate factors for hydrogen isotopic exchange of the *o*-, *m*-, and *p*-positions of methoxybenzene under analogous conditions are 2×10^4, 2.5×10^{-1}, and 5.5×10^4 respectively[25].



The marked difference in the influence of the methoxy-group on the reactivity of ferrocene and benzene shows the deep difference in the nature of the interaction of this substituent with the electronic systems of both substances†.

4. MECHANISM OF ELECTROPHILIC ISOTOPIC EXCHANGE OF HYDROGEN IN THE FERROCENE SERIES

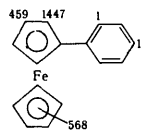
Electrophilic substitutions are characteristic of ferrocene[32]. Such a reaction capability appears clearly also in the isotopic exchange of the hydrogen atoms of ferrocene with acids[10–14]. However, the mechanism of electrophilic substitution in the ferrocene series still cannot be considered established.

In considering the mechanism of electrophilic exchange of the hydrogen of ferrocene it is necessary to settle the following questions: (1) the problem of the position of initial attack of the electrophilic reagent, (2) what are the elementary steps of the process and which of them is rate-determining, and (3) what are the nature and structure of the intermediate species and activated complex.

There is evidence that electrophilic substitution in cyclopentadienyl rings, in particular the isotopic exchange of hydrogen with acids, begins with the addition of the electrophilic reagent to the iron atom.

The formation of an addition product containing an iron–hydrogen bond by the addition of a proton to ferrocene was proved experimentally by Rosenblum and coworkers by the NMR method[12] and also by Pavlik and Šubrt by infrared spectroscopy[13]‡. Having accepted this stage as the initial one, it must be assumed that subsequent stages are the

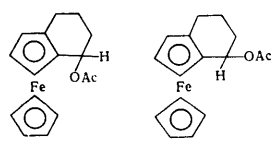
† After the present article had been sent to the press a paper appeared[81] in which values were given for the relative rate constants for the various positions of phenylferrocene in the isotopic exchange of hydrogen with trifluoroacetic acid.



Partial rate factors were determined from the change in the integral intensity of the signals of the corresponding protons in the PMR spectrum. In complete agreement with the data given above[19–21,30,31], the authors[81] concluded that the relative rates of hydrogen exchange in positions 2, 3, and 1' of ferrocene differ very little.

Pauson and coworkers[82–85] came to a similar conclusion after having investigated the aminomethylation of monosubstituted and disubstituted heteroannular derivatives of ferrocene (CH_3-, CH_3O-, and CH_3S-derivatives).

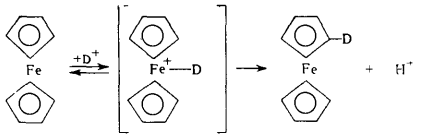
‡ The ability of the iron atom to react with electrophilic reagents agrees with other experimental results. These include, for example, data on the formation of intramolecular hydrogen bonds in ferrocenylcarbinols between the hydrogen of the hydroxyl group and the iron atom[33], between the hydrogen of a protonated carbonyl group and the iron atom in alkylferrocenylketones[34], data on the stabilisation of the carbonium centre in α-ferrocenylcarbonium ions and their conversion into radicals owing to internal single-electron transitions from the iron atom to the α-carbonium centre[35], data on the rates of solvolysis of the *endo*- and *exo*-isomers of the esters of the α-ferrocenylcarbinols A and B[36]:



endo-isomer A *exo*-isomer B

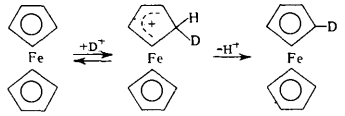
It was found that the rate of solvolysis of isomer B, in which the spatial position of the acetate group does not ensure its interaction with the iron atom (transoidal arrangement of the OAc group), is almost three orders of magnitude greater than the rate of solvolysis of isomer A, but both isomers form only the *exo*-alcohol[37].

migration of the attacking reagent into the cyclopentadienyl ring and the loss of a proton. As a result the final products of the electrophilic substitution are formed. For the isotopic replacement of hydrogen by deuterium in the action of deuterio-acids on ferrocene this final product is deuterioferrocene (scheme 1).



(1)

An alternative mechanism could be one including the immediate addition of a deuteron to the cyclopentadienyl ring (scheme 2) with the formation of a σ-complex similar to that found for aromatic compounds of the benzene series:

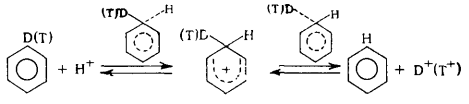


(2)

Recently kinetic isotopic effects (KIE) were used to study the mechanism of this reaction and, in particular, its rate-limiting stage. For this, the kinetics of isotopic exchange at protium of ferrocenes enriched in deuterium and tritium was investigated[38]. The following considerations applied: when the reaction proceeds by a mechanism represented in scheme 1 and its slow stage is the addition of a proton to iron and subsequent stages leading to the final product are fast, then the primary isotopic effect in this reaction should not be observed and the ratio of the rate constants of the exchange of both isotopes should approximate to unity ($k_D/k_T \simeq 1$).

On the other hand, if the reaction proceeds by a mechanism represented by scheme 2, then the kinetic isotopic effect should be observed. Actually, in the isotopic exchange of the hydrogen of benzene aromatic compounds it has been found experimentally by a large number of examples[39-42] that the ratio $k_D/k_T \simeq 2$.

The considerable KIE in the electrophilic isotopic exchange of hydrogen in aromatic compounds of the benzene series is the consequence of the difference in the rate of breaking of the C–H, C–D, and C–T bonds in the intermediate σ-complex in which the hydrogen and deuterium (tritium) atoms occupy equivalent positions (scheme 3).



(3)

However, an investigation of the kinetics of isotopic exchange of ferrocenes containing tritium and deuterium by protium when acids act on them showed that the ratio k_D/k_T here is considerably less and is 1.2[38]§. This result shows that the isotopic exchange of hydrogen in ferrocene does not proceed by mechanism 2. On the contrary, the above result agrees with mechanism 1.

However, as Hammond stated[43], the low value of the KIE can also be due to the free energies of the transition state and the intermediate compound being similar.

At the present time our information about the nature and structure of the activated complex and intermediate substances in the reaction being considered are insufficient and do not allow us to settle this question theoretically. However, in addition to the above results there are several experimental results which also support mechanism 1.

The possibility that the cyclopentadienyl nucleus exerts a specific influence on the KIE is disproved by the data obtained in studying the KIE of azulene[44]. It was shown that the KIE of azulene in electrophilic isotopic exchange of hydrogen has a normal value.

Furthermore it was found that in the protophilic substitution of hydrogen in the cyclopentadienyl rings of ferrocene in liquid ammonia with potassium amide, in which the nucleophilic reagent directly attacks the hydrogen atoms of the cyclopentadienyl rings and consequently mechanism 1 cannot occur, there is actually a significant KIE $k_D/k_T = 2.3$ (see Ref. 38).

The existence of a linear relation between the logarithm of the rate constant of the isotopic exchange of hydrogen of ferrocene and the acidity function of the medium also agrees with the fact that in the rate-determining stage of the hydrogen exchange a protonated form of ferrocene is involved.

Another fact in support of mechanism 1 is that the effect of the substituents on the redox potentials of the ferrocene–ferricinium system and on the kinetics of isotopic exchange of hydrogen in cyclopentadienyl rings is similar. This is shown by the logarithms of the rate constant of the hydrogen exchange and the logarithms of the ratio of equilibrium constants of the redox reaction of the corresponding substituted ferrocenes being linearly correlated with the same substituent constants σ_p^0.

This suggests that both reactions have the same reaction centre, probably the iron atom. Moreover, since the addition of a proton (deuteron) to the iron atom is the rate-determining stage the presence of non-equilibrium positions in the cyclopentadienyl rings will not be reflected in the kinetics of the reaction.

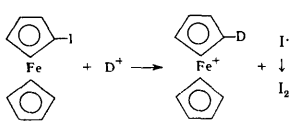
In addition it must be noted that such an explanation of the mechanism of electrophilic isotopic exchange of hydrogen in the ferrocene system encounters certain difficulties. For example, according to X-ray structural analysis the iron atom in the ferrocene compounds is shielded by the cyclopentadienyl rings (distance between the rings 3.32 Å)[45], which should hinder the approach of the attacking reagent towards it.

Quantum-chemical calculations show that the excess of electron density in the ferrocene molecule is concentrated on the cyclopentadienyl rings, and the iron atom has an excess of positive charge and consequently preferential attack of electrophilic reagents on the cyclopentadienyl rings can be expected[46,47].

The explanation of this discrepancy may be that the X-ray structural analysis and the quantum-chemical calculations consider the unexcited ferrocene molecule, present in the ground state and do not take into account the changes which occur to the molecule in the reaction process.

New facts showing the significant part played by the iron atom in the substitution were obtained[48] in studying the reaction of deuteriofluoroacetic acid with iodoferrocene.

It appeared that under these conditions the iodine is replaced by the deuteron of the acid with the simultaneous oxidation of the ferrocene to ferricinium and the detachment of the iodine as atomic iodine (scheme 4):



(4)

§ In a recent paper[86], in which a new point of view about the mechanism of electrophilic substitution in metallocenes was expressed, the value $k_H/k_D = 1.8$ was given for the hydrogen exchange of ferrocene in acid medium. If the ratio $k_H/k_D = (k_D/k_T)^{2.26}$ given by Swain and coworkers[87] is used, then $k_D/k_T = 1.3$ and consequently the values of the KIE given in Refs. 38 and 87 seem similar.

The synchronism of the processes of the replacement of iodine by a deuteron and the oxidation of ferrocene to ferrocinium shows that in the intermediate compound (or transition state) the iron atom plays an active part, with the redistribution of the electrons readily taking place in the system.

5. ISOTOPIC EXCHANGE OF THE HYDROGEN OF METALLOCENES

a. Data on the Relative Nucleophilicity of Some Metallocenes

Over sixty elements are now known to be capable of forming π-cyclopentadienyl compounds[49]. Many metallocenes have been found capable of undergoing electrophilic substitution (compounds of Fe, Mn, Re, Os, Ru, V, Cr, etc.).

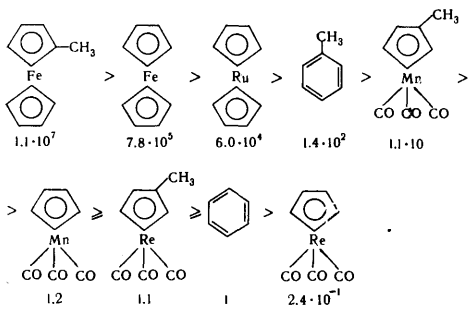
These reactions have been especially widely investigated for ferrocene, whereas other metallocenes have been considerably less studied and for many of them generally nothing is known about substitutions in the cyclopentadienyl ligands.

The failures in attempts to bring about substitution in such metallocenes are not always due to lack of reactivity but are often explained by the instability of the metallocenes under the reaction conditions.

This therefore gives rise to the quite important requirement for a sufficiently general method which will allow the reactivity of the ligands to be characterised both qualitatively and quantitatively. It was shown earlier that the isotopic exchange of hydrogen is extremely suitable for this purpose.

The possibility of changing within wide limits the acidity of the medium, on which the rate of hydrogen exchange depends to a considerable extent, allows systems which differ greatly in reactivity to be compared.

The study of the kinetics of isotopic exchange of hydrogen of certain metallocenes and their methyl derivatives and the comparison of these results with those on the isotopic exchange of benzene compounds led to the following series, in which the rate of hydrogen exchange of benzene is taken as unity and the number characterising the relative rate of hydrogen exchange of the given compound is written under its formula:



It could be expected that in other electrophilic substitutions also these systems will show approximately the same relative reactivity.

Quite recently Fischer and coworkers[50] investigated the reactions of competing Friedel–Crafts acetylation of π-cyclopentadienyl compounds of the transition metals, using the PMR method to determine the composition of the acylation products. On the basis of their results the compounds investigated are arranged in the following order of decreasing reactivity to acetylation:

$$(C_5H_5)_2Fe > CH_3OC_6H_5 > (C_5H_5)_2Ru > C_5H_5Mn(CO)_3 > (C_5H_5)_2Os > C_5H_5Cr(CO)_3NO > C_5H_5V(CO)_4 \approx C_6H_6 > C_5H_5Re(CO)_3.$$

It is essential to note that the Fischer series compiled on the basis of the qualitative data on the competing reactions of acetylation agrees completely with the series constructed on the basis of the kinetic data on the hydrogen exchange rates in acid media.

At the present moment we still do not possess the necessary facts to trace sufficiently broadly the dependence of the reactivity of the ligands on the position of the complex-forming metal in the Periodic System.

However, the results of a study of the kinetics of hydrogen exchange of the π-cyclopentadienyl compounds of the transition metals show that on going from an element of the fourth period (Mn) to an element of the sixth period (Re) in Periodic Group VII the reactivity of the π-cyclopentadienyl ligands in acid media diminishes. A similar picture is observed also for the π-cyclopentadienyl compounds of the Group VIII metals. The cyclopentadienyl derivatives of iron (fourth period) are more reactive than the corresponding ruthenium derivatives (fifth period). More detailed information on the isotopic exchange of hydrogen of some metallocenes is given below.

b. Isotopic Exchange of the Hydrogen of the Metallocenes of the Group VII Transition Metals

π-Cyclopentadienyl compounds are now known for all the transition metals of Group VII—manganese, rhenium, and technetium[51]. The greatest number of papers relate to compounds of manganese, and in particular to cyclopentadienylmanganesetricarbonyl (CMT) and its derivatives.

Electrophilic substitutions are characteristic for the cyclopentadienyl ring π-bonded to the $Mn(CO)_3$ group—alkylation[52], acylation[53], sulphonation[54], phosphorylation[55], mercuration[56], etc.

The reactivity of CMT in electrophilic substitutions was compared with the reactivity of benzene and anisole in competing acylations[57]. It was found that the compounds investigated are arranged in the following series according to their reactivity:

$$CH_3OC_6H_5 > CH_3C_6H_4Mn(CO)_3 > C_6H_5Mn(CO)_3 > C_6H_6.$$

Results which characterise the relative reactivity of CMT quantitatively were obtained in studying the kinetics of isotopic exchange of hydrogen of CMT and benzene with a mixture of deuteriated trifluoroacetic and sulphuric acids in methylene chloride solution[58].

It was found that the rate constant of hydrogen exchange of CMT is 1.3–2 times that for benzene under the same conditions.

Experiments[58] on the competing hydrogen exchange of a mixture of CMT and benzene have been described; they led to the conclusion that there was little difference in the relative reactivity of these substances.

The isotopic exchange of hydrogen with acids was used for studying the influence of alkyl substituents on the reactivity of the CMT system and these results are compared with analogous data for the benzene series (Tables 2 and 3)[59].

It appeared that the influence of electron-donating alkyl groups in CMT is much less than in benzene. The introduction of one methyl group into CMT increases the rate of

isotopic exchange of hydrogen nine times, whereas one methyl group in the benzene ring increases the rate of hydrogen exchange 155 times. Three ethyl groups in the cyclopentadienyl ring of CMT activates the deuterio-exchange less than one methyl group in the benzene ring. The rate constant of the hydrogen exchange of triethylcyclopentadienylmanganese tricarbonyl increases 126 times and the hydrogen exchange of 1,3,5-trimethylbenzene more than 7 orders. It is interesting to note that in the ferrocene series the alkyl groups activate the cyclopentadienyl ring approximately the same as for CMT. Evidently the lesser influence of the alkyl groups in the cyclopentadienyl rings of the metallocenes compared with the compounds of the benzene series has a general character and depends little on the nature of the metal connected with the cyclopentadienyl ring.

Table 2. Isotopic exchange of the hydrogen of derivatives of CMT.

Substance	Relative rate of isotopic exchange of hydrogen
$C_5H_5Mn(CO)_3$	1
$(CH_3)C_5H_4Mn(CO)_3$	9
$(C_2H_5)C_5H_4Mn(CO)_3$	5
$(C_2H_5)_2C_5H_3Mn(CO)_3$	57
$(C_2H_5)_3C_5H_2Mn(CO)_3$	126
$(C_2H_5)_4C_5HMn(CO)_3$	512
$(C_2H_5)_5C_5Mn(CO)_3$	0

Table 3. Isotopic exchange of the hydrogen of alkylbenzenes[60].

Substance	Relative rate of isotopic exchange of hydrogen
Benzene	1
Toluene	155
o-Xylene	850
Mesitylene	$135 \cdot 10^5$

It was shown recently[61] that cyclopentadienylrheniumtricarbonyl (CRT) is capable of electrophilic hydrogen exchange under the same conditions as those under which CMT undergoes this reaction.

The influence of the nature of the metals of the same group, Re and Mn, was compared by the reactivity of the cyclopentadienyl rings π-bonded with them in reactions of electrophilic isotopic exchange. The rate constants of the hydrogen exchange under the same conditions were 0.7×10^{-6} s^{-1} for CRT and 3.9×10^{-6} s^{-1} for CMT. These results show that in the reaction being considered the nucleophilic reactivity of the manganese compound is greater than that of the rhenium compound and therefore it can be expected that the rhenium compounds will also appear less reactive in other electrophilic substitutions.

On the introduction of a methyl group into the cyclopentadienyl ring of CRT the rate of electrophilic hydrogen exchange increases by approximately 5 times and consequently the activating influence of the methyl group in this system is approximately the same as in other metallocenes.

An interesting feature of the cyclopentadienyl derivatives of manganese and rhenium was their ability to undergo isotopic exchange of hydrogen in basic media (protophilic exchange) under comparatively mild conditions with ethanol in the presence of sodium ethoxide[62]. Under these conditions neither benzene nor ferrocene undergoes isotopic exchange.

An investigation of the kinetics of this reaction showed that the rhenium derivative exchanges hydrogen more rapidly than the manganese compound. The rate constant of the hydrogen exchange is 3×10^{-6} s^{-1} for CMT and 80×10^{-6} s^{-1} for CRT. It was found that exchange in alkali media, unlike electrophilic hydrogen exchange is retarded on the introduction of methyl groups into the cyclopentadienyl rings of CMT and CRT.

Hence the investigation of isotopic hydrogen exchange of cyclopentadienyl derivatives of the transition elements of Group VII showed that on going from Mn (fourth period element) to Re (sixth period element) the reactivity of the π-cyclopentadienyl ligands in electrophilic hydrogen exchange is reduced and that in protophilic is increased. The values of the relative constants of the rate of isotopic exchange are as follows:

acid medium

51.0	5.6	5.1	1.0
$CH_3C_5H_4Mn(CO)_3$	$C_5H_5Mn(CO)_3$	$CH_3C_5H_4Re(CO)_3$	$C_5H_5Re(CO)_3$
1.0	1.9	21	50

basic medium

The influence of electron-donating and electron-withdrawing substituents in the protophilic isotopic exchange was investigated in the case of monosubstituted derivatives of cyclopentadienylmanganesetricarbonyl. The overall hydrogen exchange rate constants for cyclopentadienyl ligands, which characterises their relative reactivity, are given in Table 4.[63]

Table 4. Total and relative rate constants for the isotopic exchange of hydrogen of substituted CMT compounds.

Substance	$10^4 k_{h.e.}$, s^{-1}	k_{rel}*
$C_5H_5Mn(CO)_3$	3.1	1
$CH_3C_5H_4Mn(CO)_3$	1.6	0.5
$C_2H_5C_5H_4Mn(CO)_3$	1.2	0.4
$HSO_3C_5H_4Mn(CO)_3$	8.0	2.6
$HCOOC_5H_4Mn(CO)_3$	3.4	1.1

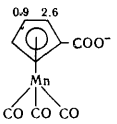
* Rate relative to the rate of exchange of CMT.

From Table 4, the influence of substituents of either donor or acceptor nature appears to be extremely weak in the cyclopentadienylmanganesetricarbonyl system.

The reason for this remarkable feature of the cyclopentadienyl system, π-bonded with a $Mn(CO)_3$ group remains vague and needs further investigation.

Very little is known about the orienting action of the substituents in the cyclopentadienyl nucleus of CMT. The only work in this field is devoted to a study of the orienting action of the carboxyl group in the CMT system in protophilic isotopic exchange[64]. The combined use of the methods of isotopic hydrogen exchange and proton magnetic resonance allowed a difference in the reactivity of the α and β positions of a carboxy-derivative of CMT to be observed. From the change in the integral intensity of the

signals of the α and β protons in the isotopic exchange the partial rate factors for exchange were determined for these positions, which were 2.6 and 0.9 for the α and β sites respectively. The ratio of the factors $f\alpha/f\beta = 2.9$ characterises the difference in reactivity of these sites:



Evidently in protophilic substitution the influence of the electron-withdrawing carboxyl group in the cyclopentadienyl ring π-bonded with the $Mn(CO)_3$ group is due mainly to an inductive effect.

c. Isotopic Exchange of the Hydrogen of Metallocenes of Transition Metals of Group VIII

As already noted, a characteristic reaction for the compounds of the ferrocene series is electrophilic hydrogen exchange, as well as other electrophilic substitutions. However, for the other Group VIII metallocenes—nickelocene and cobalticene, not even one substitution was known.

Unlike ferrocene, cobalticene and nickelocene are unstable in acid media. The rate of oxidation and decomposition of these systems evidently exceeds the rate of the substitution, as a result of which electrophilic hydrogen exchange does not exist for either cobalticene or nickelocene.

However, it was recently found that in protophilic substitution in the presence of bases nickelocene is capable of undergoing isotopic exchange of hydrogen. Thus it appeared that on treating nickelocene with diethylamine containing deuterium at the nitrogen atom, in the presence of lithium diethylamide, isotopic exchange of hydrogen takes place in the cyclopentadienyl rings of nickelocene[65]:

$$(C_5H_5)_2Ni \xrightarrow{Et_2ND,\ Et_2NLi} (C_5D_5)_2Ni\ ,$$

The rate of the hydrogen isotopic exchange of nickelocene depends on the concentration of lithium diethylamide and for example, at a lithium diethylamide concentration of 0.09 N in diethylamine solution (Et_2ND) at 25°C the rate constant of the isotopic exchange is $\sim 6 \times 10^{-5}$ s^{-1}. It is interesting to note that under these conditions neither ferrocene nor cobalticene undergoes hydrogen exchange.

Protophilic isotopic exchange of hydrogen in ferrocene has been brought about only under much more drastic conditions—in liquid ammonia in the presence of potassium amide[38].

The rate constant of the replacement of deuterium in deuterioferrocene by protium in a 0.02 N solution of potassium amide in liquid ammonia at 13°C is 9×10^{-4} s^{-1}. Under the same conditions the rate constant of the exchange of deuterium in benzene is 3×10^{-5} s^{-1}. From these results it follows that in ferrocene and benzene the hydrogen atoms exhibit considerably less acidity than in nickelocene.

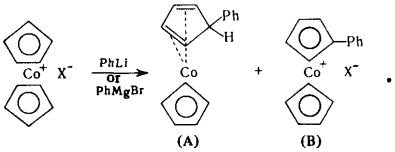
Although the hydrogen isotopic exchange of nickelocene in the presence of bases is so far the only example of substitution in this system, it can be expected that nickelocene is capable of undergoing substitution with catalysis by bases and that these reactions should proceed more readily than in ferrocene and benzene.

The replacement of hydrogen in the presence of bases could also be carried out with the isoelectronic analogue of ferrocene—the cobalticinium ion. It was found that in the reaction of cobalticinium hydroxide with deuteriomethanol in the presence of sodium methoxide cobalticinium hexachloroplatinate, isolated by treatment of the reaction products with hydrogen hexachloroplatinate, contains deuterium in the cyclopentadienyl rings[66].

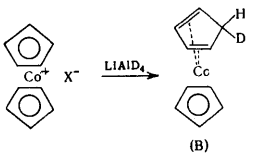
The kinetics of hydrogen isotopic exchange of cobalticinium methoxide with a 10% solution of sodium methoxide in deuteriomethanol (CH_3OD) was studied at 50°C and the rate constant of this reaction is 6.4×10^{-5} s^{-1}:

$$(C_5H_5)_2Co^+X^- \xrightarrow{CH_3OD,\ CH_3ONa} (C_5D_5)_2Co^+X^-\ .$$

An indication of the possibility of substitutions in the cyclopentadienyl rings of the cobalticinium ion was obtained earlier[67], since it was noted that with phenyl-lithium or with phenylmagnesium bromide cobalticinium salts form, as well as addition products (A), a certain proportion of phenyl-containing substitution product (B):



However, in other studies it appeared that compounds of the cobalticinium ion with nucleophilic reagents form only addition products analogous to compound A, and lithium tetradeuterioaluminate, for example, reacts with cobalticinium to form cobaltcyclopentadienylmonodeuteriocyclopentadienide (compound B) and does not form substitution products[68]:



Clearly the available information is insufficient for judging the reactivity of the cyclopentadienyl ligands in the metallocenes of nickel and cobalt, but the above examples of the replacement of hydrogen in these systems provide a basis for assuming that they are capable of undergoing other base-catalysed substitutions.

6. ISOTOPIC EXCHANGE OF HYDROGEN IN THE AROMATIC RINGS OF ARENECHROMIUM TRICARBONYLS

The simplest representative of the arenechromiumtricarbonyls—benzenechromiumtricarbonyl—was obtained by Fischer and Öfele in 1957.[69] A considerable number of representatives of this type of compound have now been listed but their reactions, and especially substitutions in the aromatic ring, have been little studied.

It has been found that electrophilic substitution in arenechromiumtricarbonyl complexes, and particularly Friedel–Crafts acetylation, takes place with much more difficulty than in the corresponding aromatic compounds[70]. However, nucleophilic substitutions take place more readily in these systems than in arenes. For example, the chlorine in chlorobenzenechromiumtricarbonyl is smoothly replaced by the methoxy-group with sodium methoxide in methanol[71]. Quantum-chemical calculations of Brown predict greater ease of nucleophilic replacement in arenechromiumtricarbonyls than in arenes, which agrees with the experimental facts.

One of the cardinal problems of the chemistry of arene complexes of transition metals is the question of how the blocking of the π-electrons of the aromatic ring by the atoms of the transition metals affects the properties of the aromatic system. In particular, it is important to find how the reactivity of an aromatic system π-bonded with a transition metal atom changes and how the electronic effects of the substituents in such systems are passed on.

It is evident that a comparison of the properties of the compounds of the series of benzene and π-arene complexes with the chromiumtricarbonyl group can give valuable information in this respect. Such a type of investigation was made, in particular, by Fischer and coworkers[70]. The Friedel–Crafts acylation of toluenechromiumtricarbonyl and toluene was compared. It was found that the content of the *o*-, *m*-, and *p*-isomers in the acylation products is quite different for toluene and its complex with chromiumtricarbonyl group. Whereas for toluene the proportions of the *o*-, *m*-, and *p*-acetyl substituents were 1.2, 2.0, and 96.8%, for toluenechromiumtricarbonyl they are 43, 17, and 40% respectively.

The much smaller difference in reactivity of the *o*-, *m*-, and *p*-positions of alkyl-substituted arenechromiumtricarbonyls in comparison with the corresponding alkylarenes in the acylation was also noted by Jackson and Jennings[73]. Fritz and Kreiter[74] came to the same conclusion on the basis of studies of the PMR spectra of disubstituted arenechromiumtricarbonyls.

Interesting possibilities for the quantitative study of the transmission of the influence of the substituent in the benzene ring π-bonded with a transition metal atom were presented after it had been observed that the hydrogen atoms in benzenechromiumtricarbonyl are capable of undergoing isotopic exchange with deuterioalcohols or deuterioamines in the presence of bases[75].

It was found that at 100°C in a 10% solution of sodium ethoxide in deuterioethanol the rate constant for isotopic exchange of the hydrogen of benzenechromiumtricarbonyl is $\sim 1.0 \times 10^{-5}$ s^{-1}. It is interesting that benzene itself under such conditions does not undergo isotopic exchange of hydrogen.

Quantitative characterisation of the effect of substituents on the reactivity of the *o*-, *m*-, and *p*-positions of the monosubstituted benzene ring π-bonded with the $Cr(CO)_3$ group were obtained by the combined use of isotopic exchange of hydrogen and proton resonance methods[76,77]. It appeared that in an aromatic ring π-bonded with the $Cr(CO)_3$ group the influence of the substituent in protophilic hydrogen exchange is extremely weak and the difference in the reactivity of the *o*-, *m*-, and *p*-positions of the ring is also very low. Table 5 shows the partial rate factors for isotopic exchange at the various positions of the aromatic ring in toluenechromiumtricarbonyl[76] and anisolechromiumtricarbonyl[77].

For comparison Table 5 also gives partial rate factors for the non-equilibrium positions in toluene and anisole found by Shatenshtein and coworkers[78] in a study of the isotopic exchange of hydrogen of these compounds in liquid ammonia in the presence of potassium amide. These results show that the influence of the methyl, and particularly the methoxyl, group in arenechromiumtricarbonyls is considerably weaker than in the corresponding arene.

Whereas the partial rate factors in anisolechromiumtricarbonyl differ by only a factor of 3, this difference is much greater for anisole.

An investigation of the isotopic exchange of hydrogen of arenechromiumtricarbonyls containing electron-donating (Me_2N–, CH_3–) and electron-withdrawing (CH_3COO–) substituents (Table 6) gave remarkable results: the overall rate constants of hydrogen exchange of arenechromiumtricarbonyls containing substituents with opposite electronic effects do not differ much[77]. Consequently, the influence of different substituents in protophilic hydrogen exchanges in arenechromiumtricarbonyls complexes is weak.

Table 5. Factors of the partial rate of isotopic exchange of the hydrogen of arenechromiumtricarbonyls and arenes.

Compound	Factors of the partial rate of hydrogen exchange			Reaction conditions	Reference
	f_o	f_m	f_p		
$CH_3C_6H_5Cr(CO)_3$	0.3	1.1	1.1	EtOD + 10%	76
$CH_3OC_6H_5Cr(CO)_3$	4.8	1.6	2.5	EtONa 100°	77
$CH_3C_6H_5$	0.2	0.4	0.4	$ND_3 + KND_2$	78
$CH_3OC_6H_5$	500	1	0.5	13°	78

It is interesting to remember that the weak influence of substituents on the reactivity of the cyclopentadienyl rings bound to the $Mn(CO)_3$ group was also noted in studying the reactions of protophilic isotopic exchange in the cyclopentadienylmanganesetricarbonyl system. Despite the fact that quantitative data characterising the reactivity of the arene complexes of chromium are even fewer, nevertheless hydrogen isotopic exchange studies on this system suggest that the electronic effect of the substituents in the benzene ring is much more pronounced than in the system where the benzene ring is π-bound with the $Cr(CO)_3$ group.

Table 6. Total rate constants of isotopic exchange of the hydrogen of arenechromiumtricarbonyls[76,77].

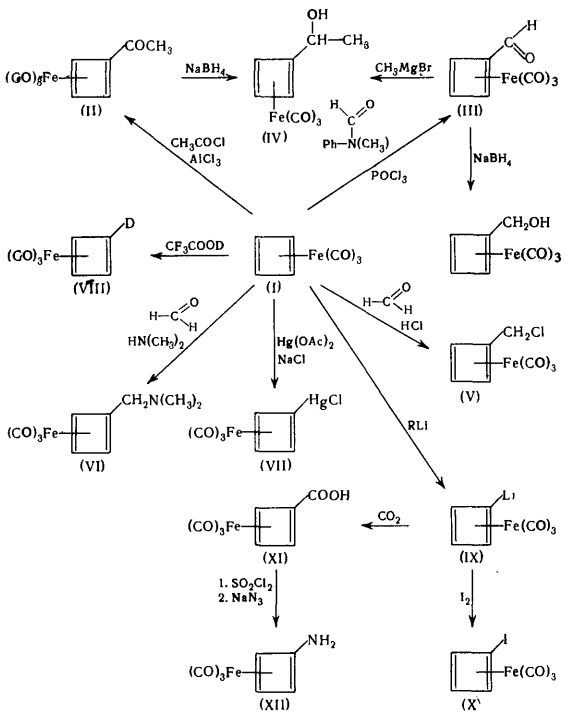
Substance	$10^5 k_{h.e.}$, s^{-1}
$C_6H_6Cr(CO)_3$	1.1
$(CH_3)C_6H_5Cr(CO)_3$	1.4
$(CH_3)_2N{-}C_6H_5Cr(CO)_3$	0.3
$CH_3OC_6H_5Cr(CO)_3$	2.8
$CH_3OCOC_6H_5Cr(CO)_3$	0.8

It is extremely probable that the levelling of the differences in the strength of the orientating action of the substituents in π-bonded aromatic ligands is a common phenomenon.

7. ISOTOPIC EXCHANGE OF HYDROGEN IN CYCLOBUTADIENEIRONTRICARBONYL

In 1965 Pettit and coworkers[79] obtained the first stable complex of cyclobutadiene with irontricarbonyl. It was found that this new complex exhibits aromatic properties and readily undergoes electrophilic substitution[80].

The authors were able to effect most of the usual electrophilic substitutions—acetylation, aminomethylation, chloromethylation, mercuration, etc. (see the scheme, I–XII).



The isotopic exchange of hydrogen with deuterium-enriched trifluoroacetic acid was also studied and it was found that even after a few minutes, in addition to the monodeuterio-derivative, more extensively deuteriated derivatives of cyclobutadieneirontricarbonyl are also formed (see the scheme, VIII).

These investigations led the authors to conclude that the reactivity of cyclobutadieneirontricarbonyl in electrophilic substitutions is very similar to the reactivity of ferrocene, both systems being considerably more reactive than benzene.

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Copper and Silver Acetylides in Organic Synthesis

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A review of the reactions of copper, silver, and gold acetylides with halides, aryl halides, unsaturated halogen compounds, diazonium salts, halides of organic acids, and organometallic compounds. Information on the structure of copper and silver acetylides and their physical properties is given. The mechanisms of the reactions of copper acetylides with the above types of compounds and the mechanism of the oxidative condensation of acetylenes are considered. The properties of copper and silver acetylides are compared with the properties of the cyanides of these metals. Bibliography of 127 references.

CONTENTS

I.	Introduction	748
II.	Acetylides of acetylene	748
III.	Structure of acetylides	750
IV.	Chemical properties of acetylides	751

I. INTRODUCTION

In 1955, Braude, in considering the progress reached in organometallic synthesis, noted two important stages—the discovery of the organomagnesium compounds by Grignard and the development by Ziegler of the chemistry of organolithium compounds. Approximately 25 years after the discovery of the organolithium compounds, Ziegler investigated the organic compounds of aluminium and introduced them into the practice of organometallic synthesis.

And now these three classes of organoelemental compounds are of importance in organometallic synthesis. In addition the unceasing search in the field of reactions of other organoelemental compounds is evidence that the use of organic compounds of other elements is necessary to solve many particular and some general problems of synthetic organic chemistry.

Even as long ago as 1959 at the VIIIth Mendeleev Conference on General and Applied Chemistry, A. N. Nesmeyanov noted that the intensive investigations of the last decade had allowed almost all the known types of organoelemental compounds to be introduced into the practice of organic synthesis; organoelemental chemistry, which had been separated as an independent branch of organic chemistry was reunited with it again on another, more modern, level.

The impression is created that there is now an accumulation of experimental material and of its generalisation in the field of the reactions and properties of many organoelemental compounds. It must be expected that the development of the chemistry of certain of these compounds will lead to the emergence of a new stage in the development of organometallic synthesis.

Of such compounds the organic compounds of copper merit attention. An investigation of the aryl and alkyl compounds of copper showed the possibility of their use in organic synthesis. However, the ethynyl compounds of copper were of the most interest, owing to their relative stability and promise of application. Copper acetylides have already come to be regarded as common reagents in organic synthesis. Oxidative condensation of acetylenes was recently examined in several extensive reviews. Information published recently about certain reactions of the copper acetylides reflects the great interest in these compounds. Evidently the acetylides of the bisacetylene derivatives present a unique possibility for the synthesis of individual poly-ynes and of polymers, the chain of which consists of conjugated carbon–carbon groupings with triple bonds.

Because of this we thought it timely to review the information on the synthesis, structure, and reactions of the copper and silver acetylides.

II. ACETYLIDES OF ACETYLENE

The first information on copper acetylides was published by Böttger[1] in 1859. On passing illuminating gas through an ammoniacal solution of copper(I) chloride he observed the formation of a cinnabar-red precipitate, explosive when dry. Some of the reactions of copper acetylide led the author to suggest that he had obtained a substance containing copper, carbon, and very little hydrogen. In particular it was found that under the action of potassium cyanide and hydrochloric acid the precipitate is decomposed with evolution of a gaseous hydrocarbon burning with a very smoky flame. Analogous compounds were obtained with salts of silver(I) and gold(I). A year later Berthelot[2] purified the hydrocarbon obtained from the copper acetylide, investigated it, and named it acetylene.

From the moment of discovery of the acetylides their intensive investigation began. Finding the composition and structure of the acetylides became the theme of a series of investigations, but immediately a large number of contradictions arose, both in the results of the experiments and also in their treatment. A detailed review of the work at the end of the XIXth century and the beginning of the XXth century was given in a monograph[3]. It seems desirable in the present review to pay attention mainly to the latest studies in this field, referring to the older studies mainly as illustrative material.

The most widespread of the methods for obtaining the copper acetylides, including also those for analytical purposes, was developed by Ilosvay[4]. He proposed reagents which stored well, prepared by the reduction with hydroxylammonium chloride of ammoniacal solutions of copper(II) chloride, sulphate, or nitrate. Keiser[5] showed that copper acetylides, unlike the silver acetylides, always contain a certain amount of elemental carbon and explained its formation by the oxidising action of atmospheric oxygen. He obtained the purest specimen of copper acetylide in the reaction of acetylene with copper hydroxide (CuOH)

suspended in water. The analyses were in complete agreement with the formula Cu_2C_2 for copper acetylide and Ag_2C_2 for silver acetylide.

Klement and Ködermann-Gros[6], who obtained copper acetylide in the absence of oxygen, consider that ammoniacal solution first deposits a non-explosive red acetylide of composition $Cu_2C_2.H_2O$, which in air is partly oxidised and loses water, being converted into a black, extremely explosive acetylide. Brameld and coworkers[7] obtained acetylides from various copper(I) salts in alkali and acid media in an atmosphere of nitrogen. The acetylides obtained in an ammoniacal medium from Cu_2Cl_2 and dried in a vacuum over H_2SO_4 and P_2O_5 had a C/Cu ratio in the range 0.94–1.2, depending on the alkalinity of the ammoniacal solution.

In Easterbrook and Erskine's comprehensive review[8] it was noted that slight variations in the method of preparation are reflected in the composition of the acetylide. The time of passing (or the flow rate) of the acetylene and the possibility of oxidation had a considerable effect. Even the dry acetylide is slowly changed on storage in the air with normal humidity, $Cu(OH)_2$ and a carbonaceous substance being formed. The authors[8] found that the copper acetylide obtained by passing acetylene into an ammoniacal solution of copper(I) salt contains on average 91–93% of an acetylide of the empirical formula $(Cu_2C_2)_2.H_2O$, 4–6% $Cu(OH)_2$, and 3–5% of a carbonaceous substance. On raising the acetylene flow rate the proportion of the carbonaceous substance is raised to 5–6%, but that of $Cu(OH)_2$ falls.

The above investigations were carried out with acetylides obtained in alkaline solutions. This is a comparatively simple example, where in the main the process is always the replacement of the acetylenic hydrogen by the metal. The reactions of acetylene with copper and silver salts in neutral or acid media are much more complicated.

The first indications of the formation of insoluble acetylenic compounds in dilute neutral aqueous solutions of Cu_2Cl_2 is in Bertholet's work[9]. Chevastelon[10] obtained the acetylide $C_2Ag_2.AgNO_3$ from neutral silver nitrate solution. The passage of acetylene into an acidified aqueous or alcoholic solution of copper(I) chloride led to the formation of colourless crystals, the composition of which was close to the formula $C_2H_2.Cu_2Cl_2$.[11] Chevastelon also isolated more complex compounds: white $C_2H_2.2Cu_2Cl_2.KCl$ and yellow $C_2H_2.4Cu_2Cl_2.2KCl$.[12]

Manchot and coworkers[13,14] found that on treatment of a hydrochloric acid solution of copper(I) chloride with acetylene a transparent solution of an addition product is formed initially, which is then converted into a violet precipitate of composition $Cu_2C_2.CuCl.H_2O$, with liberation of acetylene.

Various authors have described a large number of compounds isolated from neutral and acid solutions of silver salts but the formulae proposed for some of them (for example, $4Ag_2S_2O_3.Na_2S_2O_3.8Ag_2C_2.13C_2H_2$ [15]) raise doubts as to the individuality of the products.

The variety, and often the contradiction, in the results on the composition and structure of the acetylides reflects the complexity of the work with these substances. The explosive tendency and low solubility often do not permit the usual methods of purification to be used. At the same time the voluminous precipitates which are formed can absorb and retain firmly various impurities on the surface. The sensitivity of the acetylides to the action of oxidants and also the possibility of the conversion of the compounds formed in the presence of an excess of one of the reagents creates additional difficulties for investigators. All this evidently led in a series of instances to mixtures being described as pure substances and the adsorbed impurities being included in the composition of the acetylides.

In this connection a series of studies by Vestin and coworkers[16-24], in which the authors examine the acetylene compounds of silver and copper as analogues of sparingly soluble inorganic salts and determine the conditions of formation and existence of various compounds by measurement of equilibria, is of interest. This was usually possible. For example, by starting from the equation for the formation of silver acetylide

$$C_2H_2 + 2\,Ag^+ \rightleftarrows C_2Ag_2\,(solid) + 2\,H^+ \quad K_1 \qquad (1)$$

an expression can be written for the equilibrium constant:

$$K_1 = \frac{[H^+]^2}{[C_2H_2]\cdot[Ag^+]}.$$

When Eqn. (1) is written in the form

$$H^+ + {}^1/_2\,C_2Ag_2\,(solid) \rightleftarrows {}^1/_2\,C_2H_2 + Ag^+ \qquad (2)$$

then

$$K = \frac{[Ag]\cdot[C_2H_2]}{[H^+]} = \frac{1}{K_1}.$$

Hence

$$\lg K = \lg[Ag^+] + {}^1/_2\,\lg[C_2H_2] - \lg[H^+]$$

$$pK = -\lg K = -\lg[Ag^+] - {}^1/_2\,\lg[C_2H_2] - \lg[H^+],$$

or

$$pK = (pAg - pH) + {}^1/_2\,pP_A,$$

where P_A is the partial pressure of acetylene in the gas mixture and (pAg – pH) the difference in potentials between silver and glass electrodes. All these three quantities can be measured directly. As a result of the investigations it was shown that in ammoniacal aqueous solutions of silver salts Ag_2C_2 is precipitated but usually complexes are not formed. It is suggested that the yellow and white silver acetylides are modifications distinguished by size of the colloidal particles. Ag_2C_2 was also obtained by the reaction between dry silver acetate and acetylene:

$$2\,CH_3COOAg + HC{\equiv}CH \rightarrow 2\,CH_3COOH + AgC{\equiv}CAg.$$

Of the complex silver acetylides described earlier the individuality of the following were confirmed: $C_2Ag_2.AgNO_3$, $C_2Ag_2(AgNO_3)_6$, $C_2Ag_2.AgCl$, $C_2Ag_2.Ag_2SO_4$, and another two were obtained $C_2Ag_2.HPO_4$ and $C_2Ag_2.(AgClO_4.H_2O)_2$. All the compounds are colourless and crystallise well. The perchlorate and nitrate (1 : 1) detonate with considerable force, the others weakly.

Some authors[16-24] suggested the existence of soluble acetylene compounds of silver $(C_2Ag_2)_n.(Ag^+)_m$. The dissolution of a certain amount of acetylene in concentrated solutions of silver salts without the formation of a precipitate was noted, whereas an increase in the pH suggested the chemical bonding of acetylene. It was noted[25] that not a single silver complex is known in which the acetylene would retain both hydrogen atoms. Neither could a non-symmetrical silver acetylide be obtained[16,24]; it was shown[16] that information about the existence of complexes containing such an acetylide is unreliable. Any asymmetric copper compound of the type $HC{\equiv}CCu$ has also not been identified. The red copper acetylide obtained from ammoniacal solutions of copper salts or from dilute solutions of CuCl in an aqueous solution of alkali metal chloride

was found to have the composition Cu_2C_2 and reports of the existence of the hydrate $Cu_2C_2.H_2O$ were considered erroneous by these authors.

The complexity and variety of the compounds formed in neutral and acid media is shown by the example of the C_2H_2–CuCl–KCl–H_2O system from which no less than six solid and four dissolved compounds of acetylene can be prepared. Österlöf's[25] results on the existence of the colourless crystalline compounds $C_2H_2(CuCl)_3$ and $C_2H_2(CuCl)_2$ were confirmed.

An investigation of the violet complex, to which Chevastelon ascribed the formula $C_2H_2.Cu_2Cl_2.Cu_2O$ but Manchot and coworkers[14] $C_2Cu_2.CuCl.H_2O$, showed that this complex contains Cu_2C_2, and the ratio Cu_2C_2 : CuCl equals unity, which supports the Manchot formula. The existence of several compounds of the type $(C_2Cu_2).(CuCl)_m$ was suggested.

It was found that in a neutral concentrated solution of KCl (or NH_4Cl) and CuCl acetylene forms a yellow crystalline precipitate for which the formula $M_2[C_2(CuCl)_8]$, where $M^+ = K^+$, NH_4^+, was proposed[19]. There are grounds for considering that the violet and yellow complexes are in equilibrium:

$$Cu_2C_2 \cdot CuCl\ (solid) + 5\ CuCl + 2\ KCl \rightleftarrows K_2[C_2(CuCl)_8]\ (solid).$$

It was found subsequently that both in solution and in the solid phase compounds of two types can be formed—acetylides (bright yellow) and molecular (colourless)[20], the first in alkaline solutions, the second in neutral and acid. The results obtained suggest that in the HCl–CuCl–H_2O and HCl–$HClO_4$–CuCl–H_2O systems there are soluble complexes $CH_2.CuCl$, $C_2H_2.CuCl_2$, and $C_2H_2Cu^+$. In aqueous solutions CuCl–MCl (M = alkali metal) which contain an insignificant amount of the base, a small quantity of acetylene brings about an intense yellow coloration. The concentration of the yellow product is determined by the equilibrium, which can be written in the form:

$$C_2H_2 + n\,CuCl \rightleftarrows C_2(CuCl)_n^{-2} + 2\,H^+$$

where n lies in the range 6–8.

These results are correlated with the existence of solid complexes $M_2[C_2(CuCl)_8]$, which are readily soluble for Na^+ and Li^+, and poorly soluble for K^+ and NH_4^+.

In connection with the nature of the acetylene–metal bond it was shown[21] that copper molecular compounds of acetylene are probably close to the corresponding alkenic compounds, that is, they are π-complexes. As for the acetylenic complexes, there is only the general view that they should contain a special type of C–M bond.

The first report of the synthesis of a copper(II) acetylide belongs to Söderbaum[26]. By passing acetylene into ammoniacal solutions of various copper(II) salts he obtained a black explosive substance with the approximate molar ratio C : Cu = 2. The formulae proposed on the basis of the analytical results—the approximate $nC_6Cu_3.H_2O$ and the more accurate $nC_{17}Cu_8H_4O_3$, make it extremely doubtful that the substance is an individual and the fact that only a little acetylene is liberated under the action of hydrochloric acid, most of the carbon being converted into a humus-like substance—suggest that the product obtained is not a copper(II) acetylide.

Easterbrook and Erskine showed[8] that the precipitate obtained on passing acetylene into an ammoniacal solution of $CuCl_2$ does not contain copper(II) but is a mixture of Cu(I) acetylides and poly-ynes.

Nast and Pfab[27] obtained copper(II) acetylide in liquid ammonia by the reaction:

$$[Cu(NH_3)_4](NO_3)_2 + 2\,KC_2H \rightarrow CuC_2 + C_2H_2 + 2\,KNO_3 + 4\,NH_3.$$

The authors consider that they had isolated the compound described earlier by Söderbaum. With acid a carbonaceous residue is also formed. The only analysis for copper, made a day after obtaining the precipitate, gave a 2.7% difference from theory. We think that the results given are completely insufficient for drawing a definite conclusion about the nature of the product obtained.

By the reaction of acetylene with aqueous solutions of copper(II) salts Brameld and coworkers[7] obtained a precipitate whose composition and appearance varied with the anion, the pH of the medium, and the nature of the alkali. For products formed in ammoniacal solutions the C : Cu ratio was 2.7–2.8, for those formed in NaOH solutions, 1.99–2.07. Silvery grey, extremely explosive plates with ratio C : Cu = 2.18 separated from concentrated ammoniacal and acetic acid solutions of copper(II) acetate.

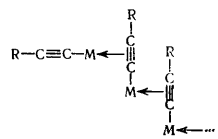
However, not one of the compounds described corresponds to the formula CuC_2—the discrepancy between the analyses and theory is always < 20%, hence here also there is also either a mixture or a compound of more complicated structure containing other components as well as C and Cu.

Feitknecht and Hugi-Carmes[28] made a detailed study of the conditions for the formation of red and black copper acetylides and even attempted to investigate the structure of these products by an X-ray diffraction method. The authors found that the acetylide precipitates obtained by Brameld and coworkers[7] from ammoniacal solutions of copper(II) sulphate and acetate, give identical X-ray diagrams, irrespective of their appearance. They did not observe bivalent copper in the acetylides obtained from solutions of copper(II) salts.

III. STRUCTURE OF ACETYLIDES

Favorskii[29] first made a cryoscopic determination of the molecular weight of copper t-butylacetylide and found that it is an octamer in benzene. The same result was obtained by ebullioscopy[30].

Calvin and coworkers[31,32] suggested that copper(I), silver(I), and gold(I) acetylides are coordination polymers in which each metal atom is π-bound with at least two acetylenic groupings. The electrons are drawn from the π_u-bonding acetylenic orbitals to the metal and from the filled d-orbitals of the metal to the unoccupied π_g-antibonding orbitals of the acetylene:



where $M^+ = Cu^+$, Ag^+, Au^+.

Both these effects should decrease the order of the C≡C bond and lead to a decrease in its frequency. Coates and Parkin[30,33] investigated the infrared spectra of copper and silver acetylides. It is known that disubstituted acetylenes absorb light in the range 2190–2260 cm^{-1}, owing to the stretching vibrations of the C≡C bond[34].

The characteristic frequency of the triple bond in the π-complex of di-t-butylacetylene with platinum is decreased[35] by 200 cm^{-1} and analogous effects are noted in transition metal complexes with alkenes[36]. In confirmation of the fact that copper acetylides are coordination polymers it was found[30,33] that these compounds absorb light in the range 1920–1960 cm^{-1}, that is, the frequency of the C≡C stretching vibrations lies 270–300 cm^{-1} lower

than in disubstituted acetylenes. The depression of the frequency is somewhat less appreciable in silver and gold acetylides (by 150–200 cm^{-1}).

The X-ray diffraction investigation of the acetylides of acetylene showed that they were crystalline but the smallness of the particles prevented any decisions concerning structure. Thus, according to the X-ray powder diagram Ag_2C_2 is a distinctly crystalline substance consisting of agglomerates of particles with a size of $> 0.1\ \mu$.[24] X-Ray diffraction data for the acetylides have also been published elsewhere[28,33].

Copper(I) and silver acetylides and cyanides have much in common. The electrons which form the coordinate bond in acetylides are the π-electrons of the acetylene groups, and in cyanides, the free pair of p-electrons of the nitrogen atom. Unfortunately, there is no information about the value of the characteristic frequency of the stretching vibrations $\nu_{C\equiv N}$ for the complexes of copper cyanide with electron-donating ligands, for which evidently an effect opposite to that observable in the infrared spectra of acetylide complexes can be expected.

Terenin and coworkers[37] showed that $\nu_{C\equiv N}$ in nitriles is increased in the formation of complexes with Lewis acids ($SnCl_4$, $AlCl_3$, etc.), copper in the cyanide can be regarded as a Lewis acid in relation to the nitrogen of the other molecule; if such an analogy is correct the release of the pair on the nitrogen should lead to a decrease in $\nu_{C\equiv N}$.

Brune and Zeil[38] consider that in nitriles the carbon of the C≡N bond group is in an sp-hybrid state, as in the acetylenes, but the nitrogen is not hybridised. In confirmation of the pair on the nitrogen having an s-character and not participating in the hybridisation as in amines the authors refer to the low basicity of the nitriles and the absence of $n \rightarrow \pi^*$ transitions in their ultraviolet spectra. Hence the σ-bond in the C≡N group will be formed by the sp-hybrid orbital of the carbon and one p-orbital of the nitrogen, but the π-bond from the C π-electrons and the N p-electrons. During coordination sp-hybridisation also appears at the nitrogen.

From quantum-chemical considerations the sp–sp bond is more stable than the sp–p bond. This is due to an increase in the strength of the bond inside the C≡N group on going from free nitrile to coordination-bound, and to the increase in $\nu_{C\equiv N}$.

However, the difference in the structure of the copper(I) acetylides and cyanide has more effect on the reactivity than on the nature of the processes which take place—copper cyanide is usually more active than acetylides in the various reactions.

IV. CHEMICAL PROPERTIES OF ACETYLIDES

1. Reactions with Formation of Acetylide Ions

The investigation of the chemical properties of the acetylides was begun by Böttger[1], who found that on treating copper acetylide with potassium cyanide a hydrocarbon is liberated, which burns with a very smoky flame. The reaction is:

$$Cu_2C_2 + 2\,KCN + 2\,H_2O \rightarrow 2\,CuCN + HC\equiv CH + 2\,KOH\,. \qquad (3)$$

In this reaction copper acetylide behaves as a sparingly soluble salt which is characterised by a definite solubility product. The bonding of the copper ions by the cyanide ions leads to a shift of the equilibrium to the right but the hydrolysis of the acetylide ion makes this process irreversible. Since the solubility product of the acetylide is scarcely greater (and usually much less) than of copper cyanide (10^{-14})[39] the occurrence of the reaction is evidently due to the formation of complex cyanides of copper $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$. The instability constants of these ions are each[40] 5×10^{-28}. An approximate calculation shows that the copper ion concentration thus created in 1 M solutions is approximately seven orders of magnitude below the Cu^+ concentration in saturated CuCN solutions. Hence, Eqn. (3) is the overall process for the following reactions:

$$Cu_2C_2 \rightleftarrows 2\,Cu^+ + C_2^{2-}, \qquad (a)$$

$$2\,Cu^+ + 6\,CN^- \rightleftarrows 2\,[Cu\,(CN)_3]^{2-}, \qquad (b)$$

$$C_2^{2-} + K^+ + H_2O \rightleftarrows C_2H_2 + 2\,KOH\,. \qquad (c)$$

Like copper cyanide, acetylides are capable of the formation of ionic complexes with acetylenic groups as ligands. Nast and coworkers obtained several such compounds by the action of alkali metal acetylides on the acetylides of copper(I),[27] silver(I),[41] and gold(I),[42] in liquid ammonia:

$$M_2\,[Cu\,(C\equiv CR)_3] \text{ and } M\,[Cu\,(C\equiv CR)_2]\,,$$

where M = Na, K; R = H, CH_3, C_6H_5;

$$K\,[Ag\,(C\equiv CH)_2] \text{ and } K\,[Ag\,(C\equiv CR)_2]\,,$$

where R = CH_3, C_6H_5; and

$$K\,[Au\,(C\equiv CH)_2],\ K\,[Au\,(C\equiv CPh)_2]\,.$$

The bifunctionality of acetylene imparts a singularity to this class of acetylide complexes, making possible the existence of μ-complexes, unknown for cyanides:

$$K_2\,[HC\equiv C—Au—C\equiv C—Au—C\equiv CH]\,.$$

An interesting complex acetylide of Cu^0 was obtained[43] by the reduction of $K_2[Cu(C\equiv CPh)_3]$ with metallic lithium in liquid ammonia and precipitation with $Ba(CNS)_2$. The infrared spectrum and diamagnetism of this compound $Ba_3[Cu(C\equiv CPh)_3]_2$ allowed its anion to be ascribed the dinuclear structure:

$$[(PhC\equiv C)_3\,Cu—Cu\,(C\equiv CPh)_3]^{6-}.$$

Whereas cyanide ions stabilise copper(II) cyanide, by forming the anionic complexes $[Cu(CN)_4]^{2-}$ the complex acetylides of copper(II) are evidently even less stable than its simple acetylenic compounds. Attempts to obtain complex acetylides of copper(II) ended in failure. In the reaction of $[Cu(NH_3)_4].(NO_3)_2$ with KC≡CH in liquid ammonia instead of the expected complex acetylide a black, very explosive precipitate is formed, which the authors consider[27] to be copper(II) acetylide, CuC_2:

$$[Cu\,(NH_3)_4]\cdot(NO_3)_2 + KC\equiv CH \rightarrow 2\,CuC_2 + C_2H_2 + 2\,KNO_3 + 4\,NH_3\,.$$

Quantitative reduction of Cu^{II} to Cu^{I} takes place with potassium methylacetylide and phenylacetylide:

$$2\,[Cu\,(NH_3)_4]^{2+} + 4\,(C\equiv C—CH_3)^- \rightarrow 2\,CuC\equiv C—CH_3 + H_3C—C\equiv C—C\equiv C—CH_3\,.$$

The reaction takes place in stages. A mixed salt of copper(I) and copper(II) is formed as an intermediate:

$$3\,[Cu\,(NH_3)_4]^{2+} + 6\,(C\equiv CPh)^- + NH_3 \rightarrow [(Cu\,(NH_3)_4]\cdot[Cu\,(C\equiv CPh)_2]_2\cdot x\,NH_3 + \\ + PhC\equiv C—C\equiv C—Ph + 8\,NH_3$$

which decomposes on distilling off the solvent, with reduction of the copper(II) and dimerisation of the acetylene radicals:

$$[Cu\,(NH_3)_4]\cdot[Cu\,(C\equiv CPh)_2]_2\cdot x\,NH_3 \rightarrow \\ \rightarrow 3\,CuC\equiv CPh + (x+4)\,NH_3 + {}^1/_2\,Ph—C\equiv C—C\equiv C—Ph\,.$$

All the complex acetylides of Cu copper(I), unlike the cyanide complexes, are extremely sensitive to moisture, which is due to the acidic properties of the alkynes being much weaker than those of even such a weak acid as HCN ($K = 4.8 \times 10^{-10}$).

2. Complexes with Electron-Donating Molecules

Like most of the compounds of copper(I), the acetylides tend to form complexes with molecules which are donors of a free pair of electrons. However, these complexes are usually considerably less stable than the corresponding derivatives of inorganic copper(I) compounds.

In liquid ammonia many acetylides form colourless insoluble ammines, stable only at low temperatures. Thus, copper phenylacetylide[27] forms the compound $C_6H_5C{\equiv}CCu.NH_3$. The analogous compound of copper cyanide, $CuC{\equiv}N.NH_3$, on being dried in a vacuum, is completely stable in dry air under ordinary conditions[44]. Copper phenylacetylide can be slowly extracted with isopropylamine[33].

Silver phenylacetylide dissolves in various amines and with isopropylamine it forms the complex $Pr^iNH_2.AgC{\equiv}C-Ph$, which rapidly loses the amine in air[31].

Gold acetylides form much more stable ammines. In the reaction of a solution of AuI in liquid ammonia—polymeric $(AuI)_n$ dissolves in liquid ammonia to form $AuI.6NH_3$—with potassium acetylide a yellow-white explosive ammine complex $Au_2C_2.xNH_3$ is precipitated, which after 4 h in a vacuum at room temperature is converted into a black-brown $Au_2C_2.xNH_3$, insensitive to moisture but extremely explosive[42]. With phenylacetylene, an aqueous ammoniacal solution of $Na_3[Au(S_2O_3)_2].2H_2O$ forms white, diamagnetic, light-sensitive $AuC{\equiv}C-C_6H_5.NH_3$, sparingly soluble only in liquid NH_3.[44]

It has been noted[27] that a suspension of dry Cu_2C_2 in liquid NH_3 is indifferent to CO. On passing dry, pure carbon monoxide into a suspension of copper methylacetylide or phenylacetylide in liquid ammonia a colourless solution of an adduct of the acetylide with CO is formed. The vaporisation of ammonia leads to the decomposition of the compound into the acetylide and carbon monoxide[45].

The copper(I) carbonyl cyanide is also unstable. With the similarly obtainable carbonyl acetylides at −79°C it decomposes with liberation of CO, even at the boiling point of liquid ammonia. Carbon monoxide is displaced from it even on blowing nitrogen through the solution[44].

A suspension of gold phenylacetylide in liquid ammonia, unlike copper phenylacetylide, does not react with CO, that is, it behaves analogously to copper acetylide[42].

On adding *p*-toluisonitrile to an ether–pyridine suspension of copper phenylacetylide at −10°C a colourless crystalline complex

$$(CH_3C_6H_4{-}N{\equiv}C)_3{\cdot}Cu{-}C{\equiv}C{-}C_6H_5$$

is formed rapidly[46]. The compound is extremely labile, is decomposed by water and organic solvents, whereas it is completely stable thermally (it decomposes at ~ 100°C). Keeping in air leads to a decomposition of the complex in a few hours. The loss of isonitrile molecules takes place even under the action of dry ether at room temperature. In aqueous pyridine at 0°C the complex dissolves with liberation of CO, since hydration of the isonitrile molecule takes place simultaneously with the decomposition:

$$C_7H_7{-}N{\equiv}C \xrightarrow{H_2O} CO + C_7H_7{-}NH_2 \xrightarrow{C_7H_7N{\equiv}C} C_7H_7{-}NH{-}CH{=}N{-}C_7H_7 .$$

It is especially interesting that there is an analogy between the other complexes of the acetylides, the reaction of the isonitrile complex of the phenylacetylide with chloroform, dissolution in which is accompanied by rapid replacement of the phenylacetylene residue by chlorine:

$$(Ar{-}N{\equiv}C)_3\,Cu{-}C{\equiv}C{-}C_6H_5 \xrightarrow{CHCl_3} (Ar{-}N{\equiv}C)_3 \cdot CuCl .$$

Copper, silver, and gold acetylides form stable complexes with tertiary phosphines, arsines, and stilbines. Coates and coworkers[30,31,33,47] synthesised and studied a large number of such complexes. The stability of these complexes, which is sharply contrasted with the instability of the ammine and amine complexes, was attributed by the authors to the ability of phosphorus and its analogues to back coordination owing to the vacant *d*-orbitals. Depending on the ratio of the components, compounds with a different number of ligands belonging to one metal atom can be obtained. The maximal number is three but the only complex of this composition:

$$PhC{\equiv}C{-}Cu\cdot(PMe_3)_3$$

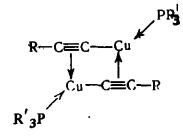
was unstable in solution, which did not allow its molecular weight to be determined. As the cryoscopic investigations showed, complexes with two ligands,

$$Bu^t{-}C{\equiv}CCu\cdot(PMe_3)_2 \text{ and } Ph{-}C{\equiv}C{-}Cu\cdot(PMe_3)_2$$

are monomeric in benzene, but the monophosphinic complexes:

$$Bu^t{-}C{\equiv}CCu\cdot PMe_3,\ Ph{-}C{\equiv}CCu\cdot PMe_3,\ Ph{-}C{\equiv}CCu\cdot PEt_3 \text{ etc.}$$

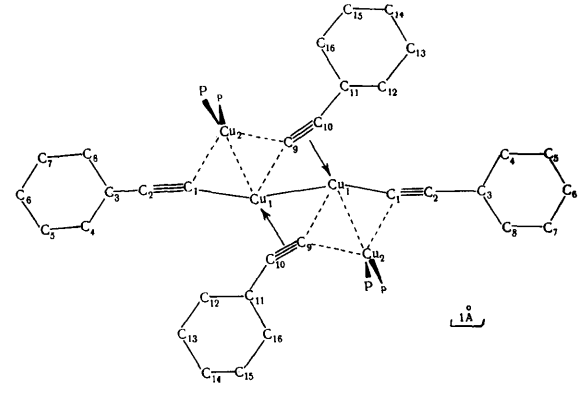
are dimeric in nitrobenzene. The authors suggest that the dimeric complexes are constructed in the following manner:



Coates and Parkin[30] give the results of an X-ray structural investigation of the complex

$$(PhC{\equiv}C{-}Cu\cdot CuPMe_3)_4.$$

Each tetrameric cell contains a zig-zag of four copper atoms. With the exception of phosphinic groups lying above and below the plane of the diagram, the structure of the tetramer is almost planar. Atoms $C_{(4)}$ and $C_{(5)}$ remain 0.2 Å from the *X*–*Y* plane of the diagram, but $C_{(7)}$, $C_{(8)}$, $C_{(15)}$, and $C_{(16)}$, 0.3 Å. The departure of all the other atoms along the *Z*-coordinate averages 0.06 Å. The benzene ring is only slightly inclined to the *X*–*Y* plane. The Cu–Cu distance ($Cu_{(1)}$–$Cu_{(1)}$ = 2.7 Å, $Cu_{(1)}$–$Cu_{(2)}$ = 2.45 Å) is almost the same as in metallic copper.



The monophosphinic complexes of silver acetylides are also not monomeric. For example, Rh–C≡CAg.PEt_3 is dimeric in nitrobenzene, and for it a structure analogous to that given above is proposed. Unlike the compounds of copper and silver the monophosphinic derivatives of gold acetylides are monomeric, which is explained by the relatively low tendency of Au^+ to an increase in the coordination number above 2. The degree of association of the phosphinic complexes can be varied within wide limits, depending on the composition of the complex, its concentration, and the nature of the solvent. Thus Ph–C≡CCu.PEt_3 is trimeric in nitrobenzene and has a degree of association from 3.3 to 3.8 (depending on the concentration) in benzene.

Unexpected properties destroying the concept of the monophosphinic complexes as coordination unsaturated compounds and therefore associated in solutions, were displayed by p-$O_2NC_6H_4$–C≡CCuPPh_3. It was monomeric in nitrobenzene. In the solid state it could be obtained in two different forms—bright red and orange, having identical composition. In benzene it is dimeric, that is, behaves similarly to many other complexes of similar structure. Monomeric diphosphinic complexes are usually coloured more than weakly associated compounds. For example, the octamer Bu^t–C≡C–Cu is orange-red[29], the dimeric Bu^t–C≡CCu.PMe_3 is yellow-green[30], but the monomeric Bu^t–C–CCu.$(PMe_3)_2$ is colourless[30]. The phosphinic complexes of copper acetylides are completely stable thermally (most of them melt without decomposition at temperatures up to 150°C) but gradually decompose on storage in air. The complexes of the diacetylenes seemed unexpectedly stable in this respect. Whereas Ph–C≡CCu.PEt_3 is converted into yellow amorphous Ph–C≡CCu after standing in air for 1–2 days, Ph–C≡C–C≡CCu.PEt_3 remains unchanged after a week.

The complexes of silver acetylides with phosphines decompose more rapidly on access of air and also in the light.

3. Reactions with Halogens and Halogenoacetylenes

Even Böttger[1] in studying the chemical properties of copper acetylide found that the reaction with chlorine is explosive, $CuCl_2$, HCl, and carbon being formed. In reacting with Br_2, or on grinding with I_2, copper acetylide ignites and carbon is liberated. On reacting silver acetylide with iodine in ether, Berend[48] obtained di-iodoacetylene. Bayer[49] found that a mixture of di-iodoacetylene and di-iododiacetylene is obtained from copper acetylide under these conditions. By the reaction of an aqueous suspension of copper acetylide of propargyl alcohol with iodine, Lespieau[50] obtained iodopropargylic alcohol:

$$HO{-}CH_2{-}C{\equiv}C{-}Cu + I_2 \rightarrow HO{-}CH_2{-}C{\equiv}CI + CuI\,.$$

It is interesting to compare the reaction of halides with acetylenic derivatives of various metals and the reaction of halides with copper acetylides. It is known that during the action of halides on the acetylenic derivatives of various metals the metal is replaced by halogen[48,51–57]:

$$BrMgC{\equiv}CMgBr + 2\,X_2 \rightarrow XC{\equiv}CX + 2\,MgBrX,(X{=}I,\ Br),$$
$$RC{\equiv}CMgBr + X_2 \rightarrow RC{\equiv}CX + MgBrX,(X{=}I,\ Br),$$
$$(RC{\equiv}C)_2Hg + 2\,Br_2 \rightarrow 2\,RC{\equiv}CBr + HgBr_2,$$
$$AgC{\equiv}CAg + 2\,I_2 \rightarrow IC{\equiv}CI + 2\,AgI,$$
$$RC{\equiv}CNa\ (K,\ Li) + Cl_2 \rightarrow RC{\equiv}CCl + NaCl\ (KCl,\ LiCl).$$

In all these instances the interaction proceeds as a competition of the halogen with the metal for the redistribution of electrons of the existing metal–carbon bond since the metals (excluding silver) are found in their highest oxidation states.

For copper acetylides, in addition to the analogous process:

$$R{-}C{\equiv}C{-}Cu + X_2 \rightarrow R{-}C{\equiv}C{-}X + CuX$$

there is another possibility—oxidation of Cu^+ to Cu^{2+}. Unlike univalent copper, bivalent copper is a typical transition metal. It could be expected that the Cu–C σ-bond in the compounds being formed, as in most compounds of metals with an incomplete d-level, will be weak and easily broken with formation of a new compound of Cu^+ or Cu^{2+} and an acetylenic radical:

$$RC{\equiv}CCu \longrightarrow [RC{\equiv}C\overset{\cdot}{)}Cu^{+}\ X^{\cdot -}] \longrightarrow RC{\equiv}C^{\cdot} + CuX + X^{\cdot},\ (\text{or } CuX_2)$$

$$2RC{\equiv}C^{\cdot} \longrightarrow RC{\equiv}C{-}C{\equiv}CR\,.$$

The weakness of such σ-bonds is explained by the similarity in energy of the electrons of the bond and the d-electrons of the metal[58]. The ease of interaction here must depend on the properties of the acetylide as a base and the halogen as a Lewis acid. The strengths of the halogens as Lewis acids change in the order

$$F_2 > Cl_2 > Br_2 > I_2.$$

This is well illustrated by the relative rates of addition of the halogens and interhalogen compounds at a double bond[59]:

I–I	1	I–Br	3000	I–Cl 100 000
		Br–Br	10 000	Br–Cl 4 000 000 .

In the molecule of the acetylide the electron-accepting groupings at the C≡C bond should hinder the removal of the d-electron of copper and electron-donating ones facilitate it.

Actually it was found[60,61] that in the reaction of copper acetylide with iodine—a weak Lewis acid, at room temperature only iodoacetylenes are formed. The reactions evidently proceed through a four-centre state of the type:

$$R{-}C{\equiv}C{-}Cu \cdots \overset{\delta+}{X} \cdots \overset{\delta-}{X}\,.$$

The simplicity of the experiment, the possibility of using acetylides with different functional groups and the high yields of iodoacetylenes allow this reaction to be regarded as a convenient preparative method for making iodoacetylenes.

By introducing iodine monobromide into the reaction it was shown that the final product is determined by the initial polarisation of the reacting molecules:

$$C_6H_5{-}\overset{\delta-}{C}{\equiv}\overset{\delta+}{C}{-}Cu + \overset{\delta+}{I}\,\overset{\delta-}{Br} \rightarrow C_6H_5C{\equiv}C{-}I + CuBr\,.$$

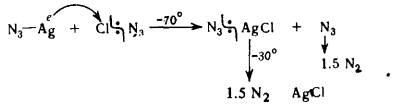
Actually, iodophenylacetylene acetylene was obtained in 60% yield.

Even at low temperatures, bromine oxidises more than half copper phenylacetylide to diphenylbutadiyne—the yield of bromophenylacetylene is $\gtrsim$ 40%. Copper p-nitrophenylacetylide gives under these conditions ~ 70% p-nitrobromophenylacetylene and only traces of di-(4-nitrophenyl)-butadiyne[61–63]. Hence acetylides with electron-withdrawing substituents at the triple bond can give bromoacetylenes in high yields.

The yield of chlorophenylacetylene from the action of a carbon tetrachloride solution of chlorine on copper phenylacetylide does not exceed 20%.

The possibility of an oxidation is also not ruled out for silver acetylides. It is known, for example, that silver

azide reacts with chlorine azide at −70°C with the formation of silver(II) azide chloride, which decomposes when the temperature is raised to −30°C to give silver chloride and molecular nitrogen[64]. The reaction is interesting in that with an obvious analogy with the oxidising action of halogens on copper acetylides an intermediate compound of the bivalent metal is fixed:



However, the bivalent state is not very characteristic for silver and is achieved only in the reaction of its compounds with very strong oxidants.

Since the ethynyl group exhibits a strong *I*-effect, the appearance of quasi-halide properties can be expected from the halogenoacetylenes, in particular the ability to play the part of strong electrophilic reagents. The dipole moments of the monohalogenoacetylenes[65] show that the electron-withdrawing properties of ethynyl and the halogens in these compounds are of the same order of magnitude:

$$HC{\equiv}CF \quad 0.75\ D\ ,$$
$$HC{\equiv}CCl \quad 0.44\ D\ ,$$
$$HC{\equiv}CBr \quad 0.00\ D\ .$$

The result of the electrophilic substitution, as for the halogens and interhalogen compounds, will be determined by the initial polarisation of the halogen derivative, for example[66,67]:

$$2\,R{-}C{\equiv}C{-}MgX + \overset{\delta+}{I}C{\equiv}C\overset{\delta-}{I} \rightarrow 2\,R{-}C{\equiv}C{-}I + XMgC{\equiv}CMgX\,,$$
$$R{-}C{\equiv}C{-}MgX + \overset{\delta-}{Cl}C{\equiv}C\overset{\delta+}{Cl} \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}Cl + MgXCl\,.$$

Actually, it was found[68] that di-iodoacetylene reacts with copper acetylides in the same way as with organomagnesium compounds:

$$2\,R{-}C{\equiv}C{-}Cu + IC{\equiv}CI \rightarrow 2\,R{-}C{\equiv}C{-}I + CuC{\equiv}CCu\,.$$

It was also shown[68] that the copper is replaced by iodine in reactions of the acetylides with di-iodoacetylene and iodonitroform $IC(NO_2)_3$.

The reaction of bromoacetylenes with acetylenes in the presence of catalytic amounts of CuCl, dissolved in the primary amine, and of a small quantity of reductant ($NH_2OH.HCl$) was proposed by Chodkiewicz and Cadiot[69] as a method for the synthesis of non-symmetrical diacetylenic compounds. Although the overall process is expressed by the equation:

$$R{-}C{\equiv}CH + BrC{\equiv}CR' \rightarrow R(C{\equiv}C)_2R' + HBr$$

the reaction actually proceeds between bromoacetylene and the acetylide[70]:

$$R{-}C{\equiv}CH + Cu^{+} \rightarrow R{-}C{\equiv}C{-}Cu + H^{+}\,, \qquad (4)$$
$$R{-}C{\equiv}C{-}Cu + Br{-}C{\equiv}C{-}R' \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R' + CuBr\,. \qquad (5)$$

There is also the side-process of condensation of the bromoacetylene under the action of Cu^{+} ions:

$$2\,R'{-}C{\equiv}C{-}Br + 2\,Cu^{+} \rightarrow R'{-}C{\equiv}C{-}C{\equiv}C{-}R' + 2\,Br^{-} + 2\,Cu^{2+} \qquad (6)$$

which is thought to proceed through the following two stages:

$$R'{-}C{\equiv}C{-}Br + 3\,Cu^{+} \rightarrow R'{-}C{\equiv}C{-}Cu + Br^{-} + 2\,Cu^{2+}\ (\text{slow})\,, \qquad (7)$$

$$R{-}C{\equiv}C{-}Cu + Br{-}C{\equiv}C{-}R' \rightarrow R'{-}C{\equiv}C{-}C{\equiv}C{-}R' + Cu^{+} + Br^{-}\ (\text{fast})\,. \qquad (8)$$

The formation of the dimer ($R'{-}C{\equiv}C{-}C{\equiv}C{-}R'$) from the acetylide can be explained by the oxidising action of the Cu^{2+} ions which are produced in reaction (6), or by the replacement of the copper in the acetylide by halogen under the action of the halogenoacetylene. The halogenoacetylene obtained can undergo condensation (6) just like the initial one. It is possible for both these processes to proceed simultaneously. A thorough survey of the Cadiot–Chodkiewicz condensation and also extensive data on its practical application have been given in a review[70].

It was found[68] that in the reaction of bromoacetylenes and iodoacetylenes ($R{-}C{\equiv}C{-}X$) with copper acetylides ($R'{-}C{\equiv}C{-}Cu$), introduced in stoichiometric amounts, a mixture of three diynes is formed:

$$R{-}C{\equiv}C{-}C{\equiv}C{-}R',\quad R{-}C{\equiv}C{-}C{\equiv}C{-}R \quad \text{и} \quad R'{-}C{\equiv}C{-}C{\equiv}C{-}R'.$$

For example, from a reaction mixture of bromophenylacetylene with copper *p*-bromophenylacetylide in dimethylformamide the products diphenylbutadiyne, 1-*p*-bromophenyl-4-phenylbutadiyne, and di-(*p*-bromophenyl)butadiyne were isolated.

The similarity in the chemical properties of copper cyanide and acetylides is observed in the reaction of CuCN with iodo- and bromo-phenylacetylenes. It was shown[62] that this results in the formation of phenylpropiolonitrile in ~40% yield. When the iodophenylacetylene was used, diphenylbutadiyne was also isolated from the reaction mass. The formation of diphenylbutadiyne during the synthesis of phenylpropiolonitrile from iodophenylacetylene and copper cyanide could be the result not only of condensation under the action of Cu^{+}, but also of the exchange of copper and halogen between the initial components.

4. Reactions with Aromatic and Unsaturated Halogen Derivatives

Friedman and Schlechter[71] found that aryl chlorides and bromides in boiling dimethylformamide react with copper(I) cyanide to form nitriles in yields from 80% to quantitative:

$$ArX + 2\,CuCN \rightarrow (ArCN)_2{\cdot}CuX + CuX\,,$$
$$(ArCN)_2\,CuX \xrightarrow{H^{+}} 2\,ArCN + CuX\,.$$

The similarity between the copper acetylides and cyanide led the authors of the present review to investigate the possibility of the introduction of acetylenic groups into the aromatic nuclei in an analogous way. It was found[60] that when aryl iodides are boiled with copper acetylides in dimethylformamide for 8–16 h disubstituted acetylenes are formed in 30–70% yield:

$$ArC{\equiv}C{-}Cu + Ar'I \rightarrow Ar{-}C{\equiv}C{-}Ar' + CuI\,.$$

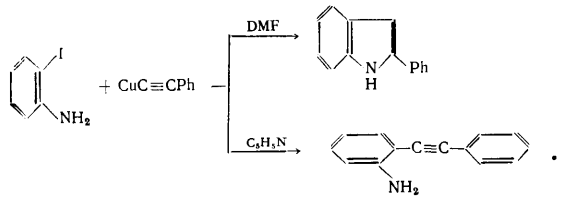
Aryl iodides with various functional groupings (nitro-, amino-, hydroxy-, etc.) can be used in the synthesis. In di-iodoaryl compounds one or both of the iodine atoms can be replaced by acetylenic radicals. Boiling a suspension of copper *p*-iodophenylacetylide in dimethylformamide leads to its autocondensation into the acetylide of 4-iodo-4-ethynyltolane.

This reaction was described simultaneously and independently by Castro and Stephens[72,73], who synthesised several tolanes in yields of 70–90% by the reaction of *para*- and *ortho*-substituted derivatives of iodobenzene with copper phenylacetylide in boiling pyridine:

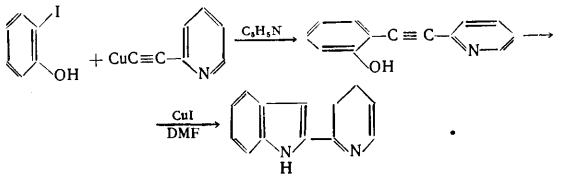
$$ArI + CuC{\equiv}CPh \rightarrow Ar{-}C{\equiv}C{-}Ph + CuI\,.$$

Heterocyclic compounds were obtained from some of the *ortho*-substituted derivatives in the same high yields. Further investigations[74] showed that this reaction is a general method for the synthesis of tolanes, indoles,

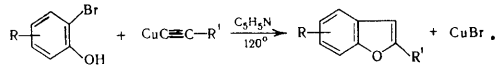
benzofurans, and phthalides. For the *ortho*-amino-derivatives the direction of the reaction is determined by the solvent: in dimethylformamide an indole is formed; in pyridine, either only an *o*-aminotolane, or a mixture of both products, depending on the acetylide:



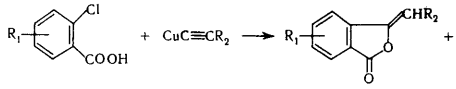
The reaction proceeds in two stages: substitution and cyclisation. The second stage takes place only in the presence of copper salts:



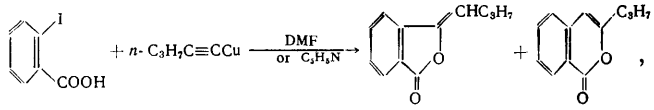
The synthesis of benzofurans proceeds easily in pyridine. Halogenophenols react more vigorously than the corresponding anilines. This allows the more stable *o*-bromophenols to be used as starting compounds:



Halogenobenzoic acids are a group of most reactive substances. Here the use of even chloro-derivatives is possible and the formation of phthalides occurs even at room temperature both in dimethylformamide and in pyridine:

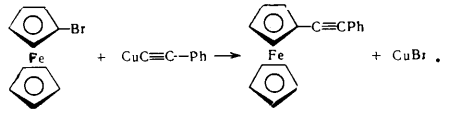


Only in one instance was the formation of isocoumarin noted as well as the phthalide:



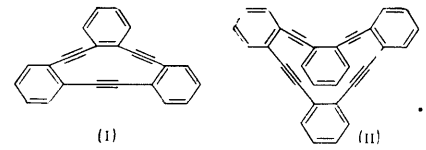
The simplicity of the behaviour and the high yields of the final products made this reaction a convenient preparative method for obtaining various acetylenic derivatives with aromatic substituents.

Nesmeyanov and coworkers[75] extended it to halogen derivatives of ferrocene. Whereas aryl bromides do not react with copper acetylides, on boiling bromoferrocene for three hours with copper phenylacetylide in a medium of dimethylformamide, ethynylphenylferrocene was formed in 48% yield:



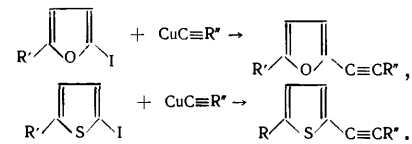
By starting from iodoferrocene, Rausch and coworkers[76] obtained the same product in 84% yield.

Campbell and coworkers[77] isolated cyclic condensation products from the pyridine solution after heating copper *o*-iodophenylacetylide—mainly the trimer (I) and a little tetramer (II):

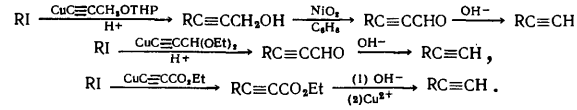


(I) (II)

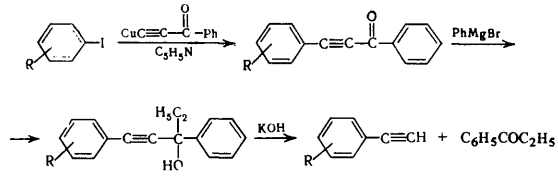
The work of Atkinson and coworkers[78,79] was devoted to the production of the acetylene derivatives of furan and thiophen:



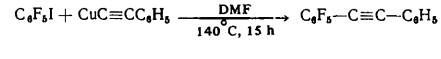
Monosubstituted arylacetylenes were also synthesised. The authors used the tetrahydropyranyl group (THP) for the protection of the hydroxyl group in the acetylides of propargyl alcohol:



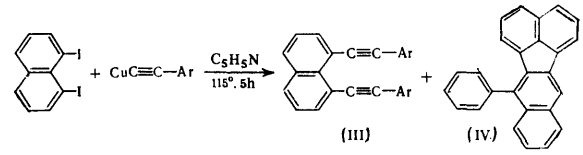
Shvartsberg and coworkers[80] developed another way of obtaining the monosubstituted arylacetylenes:



Filler and Heffern[81] carried out the reaction with pentafluoroiodoacetylene:



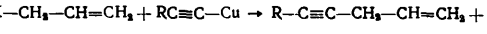
By studying the intramolecular reaction of closely situated triple bonds, Ipaktschi and Staab[82] synthesised a series of 1,8-substituted naphthalenes from 1,8-di-iodonaphthalene and copper acetylides:



(III) (IV)

Here in addition to the colourless product (III) its yellow isomer (IV) was formed. The yield of (IV) from the copper phenylacetylide was 19.5% and rose to almost quantitative on continuing boiling.

Colonge and Falcotet[83] obtained acetylenic and ethylenic alcohols by the reaction of allyl chloride and bromide or propargyl chloride (and their alkylated derivatives) with acetylides of propargyl alcohol or methylbutynol. The reaction was carried out in an aqueous solution of ammonium chloride:



where R = CH_2OH.

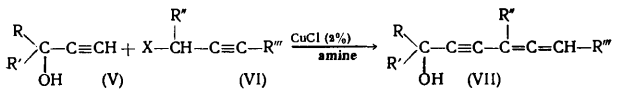
Somewhat later Kurtz[84] reproduced the same reaction but in an aqueous alcoholic solution of sodium chloride:

$$H_2C{=}CR{-}CH_2Cl + HC{\equiv}C{-}R' \xrightarrow[NaCl]{Cu+,\ H_2O} H_2C{=}CR{-}CH_2{-}C{\equiv}CR' + HCl$$

a	*b*	*c*	*d*
R=H	R=CH_3	R=H	R=CH_3
R'=CH_3	R'=C_2H_5	R'=H	R'=H

Hepta-5-en-2-yn-1-ol and 5-methylhepta-6-en-2-yn-1-ol were obtained from the acetylide of propargyl alcohol. The yields were from 29 to 90% at 70–80°C and a reaction time of 7–8 h.

On using amines as a medium for the same reaction and ethynyl carbinols as the acetylenic component, Sevin[85] employed catalytic quantities of CuCl, and observed the isomerisation of the propargyl group into allenyl:



(X = Cl or Br)

(V)	*a*	*b*	*c*	(VI)	*a*	*b*	*c*
R	H	CH_3	CH_3	R''	H	CH_3	H
R'	H	H	CH_3	R'''	H	H	CH_3

The activity of amines in reactions for the condensation of propargyl halides with ethynylcarbinols in the presence of copper(I) chloride falls in the order NH_3 > primary > > secondary > tertiary. The author suggests that the reaction proceeds by a six-centre cyclic mechanism.

Allyl halides also react with copper acetylides in boiling dimethylformamide, forming a substitution product with yields of up to 40% on the acetylide taken[60].

$$CH_2{=}CH{-}CH_2X + Cu{-}C{\equiv}C{-}R \rightarrow CH_2{=}CH{-}CH_2{-}C{\equiv}C{-}R + CuX\,.$$

For the acetylide to react completely, a large excess (up to 100%) of the allyl halide is necessary. In the presence of a catalytic amount of copper powder the reaction takes 5–15 min. The reaction proceeds readily with high yields in liquid ammonia at −33°C.

Propargyl chloride reacts no less vigorously with copper acetylide[68] on heating in dimethylformamide above 70°C. However, the products formed under these conditions are polymerised and low-molecular-weight individual substances cannot be isolated. The use of liquid ammonia instead of dimethylformamide in the reaction of copper phenylacetylide with propargyl chloride allowed a little of a hydrocarbon of composition $C_{11}H_8$ to be obtained in subsequent high vacuum distillation. On the basis of the infrared spectra it was ascribed the cumulene structure $C_6H_5{-}CH{=}C{=}C{=}CH_2$.

The ability of halogen as an isolated double bond to react with copper acetylides was studied by the example of *trans*-di-iodoethylene[86]. Copper acetylides react with di-iodoethylene more readily than with aryl iodides. Depending on the ratio of the reagents and the duration of the reaction, mono- or di-substituted products can be isolated in yields up to 65%.

$$R{-}C{\equiv}C{-}Cu + ICH{=}CHI \rightarrow RC{\equiv}C{-}CH{=}CHI + CuI\,,$$
$$2\,R{-}C{\equiv}C{-}Cu + ICH{=}CHI \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}C{\equiv}C{-}R + 2\,CuI\,.$$

The reaction takes place without change in the configuration of the *trans*-di-iodoethylene. To replace the first iodine atom it is sufficient to boil the reagents for 10–15 min. About 2 h is needed to replace the second atom.

Copper(I) cyanide also reacts analogously to the acetylides with di-iodoethylene, forming fumarodinitrile.

Burdon and coworkers[87] also reacted dihalogenoethylenes with copper acetylides in dimethylformamide or pyridine and obtained enyne and endiyne compounds in yields of up to 90%:

$$R{-}C{\equiv}C{-}Cu \xrightarrow[1\text{–}12\ h;]{40\text{–}100^\circ} \begin{cases} \xrightarrow{ICH{=}CHCl} R{-}C{\equiv}C{-}CH{=}CHCl \\ \xrightarrow{ICH{=}CHI} R{-}C{\equiv}C{-}CH{=}CH{-}C{\equiv}C{-}R\,. \end{cases}$$

The activity of the halogen at an sp^2-carbon atom increases in the order I > Br > Cl; fluorine does not react.

It can be assumed that the reaction of copper acetylides with iodoaryl and halogen derivatives containing multiple bonds takes place through an intermediate complex. The bond with the metal in this complex can be effected by the π-electrons of the halogen derivative molecules. The absence of an interaction between alkyl halides and copper acetylides supports this assumption.

The reactivity of a halogen derivative can be determined by its basicity in relation to the copper atom of the acetylide. Only indirect data can be produced to explain the results from this viewpoint.

It is known that alkylalkenes exhibit in relation to a proton much more basic properties than aromatic hydrocarbons or conjugated alkenes[88]. If this dependence is also valid for the complex formation of halogeno-derivatives with a transition metal the drop in reactivity in the sequence

$$ICH{=}CHI > ICH{=}CH{-}C{\equiv}C{-}R > ArI$$

is completely regular.

The polarisability of the halogen atom can also play a significant part in reactions of this type. From the Table it is clear that the least reactive allyl halides, aryl chlorides and bromides have the highest dipole moments, that is, they are more difficult to polarise.

The possibility of a change in the valency of copper during the interaction also cannot be excluded. Silver phenylacetylide, for which a change in the valency of the metal under these conditions is improbable, dissolves when heated in pyridine with di-iodoethylene, but does not react.

5. Reaction with Acid Chlorides

Nef[89] reported that on dissolving silver phenylacetylide in benzoyl chloride and boiling the resulting solution, phenylpropiolophenone is formed. The reaction cannot be performed with large quantities of materials since it can take place very violently.

Davis and Scheiber[90] observed that some silver alkylacetylides dissolve in CCl_4, $CHCl_3$ or benzene. By the interaction of such acetylides with various acid chlorides in carbon tetrachloride they obtained the corresponding ketones in yields of up to 72%. It appeared that these reactions are catalysed by Lewis acids. For example, silver n-butylacetylide does not react with benzoyl chloride without a catalyst, but in the presence of $AlCl_3$ n-butylpropiolophenone is formed in 72% yield:

$$n\text{-}C_4H_9{-}C{\equiv}C{-}Ag + Cl{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \xrightarrow[CCl_4]{AlCl_3} n\text{-}C_4H_9{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + AgCl\,.$$

Crombie and Griffin[91] used this method for obtaining intermediates in the synthesis of certain derivatives of

unsaturated acids. The reaction was carried out with the acid chlorides of the partial esters of dicarboxylic acids:

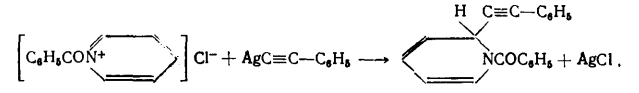
$$R{-}C{\equiv}C{-}Ag + ClCO[CH_2]_n COOMe \rightarrow R{-}C{\equiv}C{-}\overset{\overset{O}{\|}}{C}[CH_2]_n COOMe + AgCl.$$

The yields of the ketones were 30–35%.

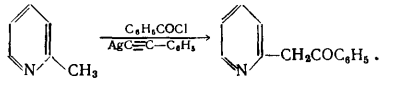
Additional moments of halogen derivatives.

X	Dipole moment, D		
	CH_3CH_2X	$CH_2{=}CHX$	C_6H_5X
Cl	2.05	1.44	1.73
Br	2.02	1.41	1.71
-	1.90	1.26	1.50

Interesting work by Agawa and Miller [92] disclosed new synthetic possibilities of reaction of silver acetylides with acid chlorides. These authors found that pyridine introduced into the reaction medium (CCl_4) becomes, in the form of an acylpyridinium salt, the main object of the nucleophilic attack of the silver acetylide. As a result of the reaction α-ethynyl derivatives of *N*-acyl-1,2-dihydropyridines are formed in yields of up to 70%:



Analogous products were also obtained with quinoline. The acetylenic ketones present as impurity did not exceed 15%. Reaction between 2-picoline, benzoyl chloride, and silver phenylacetylide takes place with the formation of 2-phenacylpyridine, AgCl, and probably phenylacetylene:



The first report of the synthesis of α-ethynylketones from acid chlorides and copper arylacetylides was published recently [93]; the yields were 40–60%:

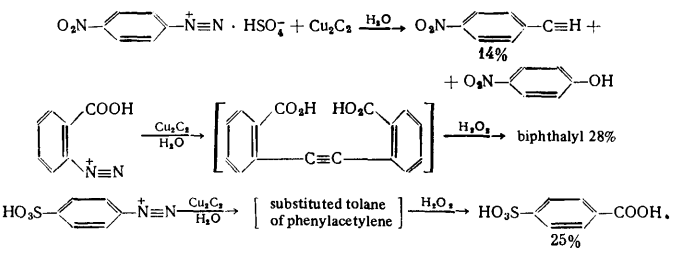
$$R{-}COCl + Cu{-}C{\equiv}C{-}C_6H_5 \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}C{\equiv}C{-}C_6H_5 + CuCl$$

where R = C_6H_5, *p*-BrC_6H_4, *p*-$O_2NC_6H_4$, *m*-$O_2NC_6H_4$, mesityl.

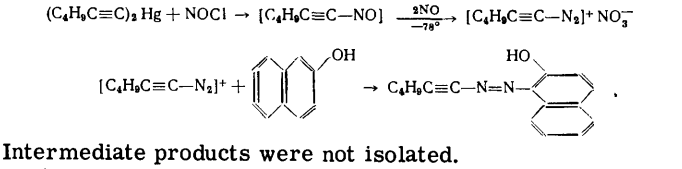
Bifunctional acid chlorides (terephthalyl chloride and isophthalyl chloride) react analogously. The reaction was carried out with the successive action of triethylamine, and then pyridine in a medium of dioxan, dichloroethane, or benzene. In the presence of only triethylamine, or only pyridine, and also in a medium of pyridine or dimethylformamide the formation of acetylenic ketones was not observed.

6. Reactions with Diazonium Salts

Sandmeyer [94] studied the reaction of copper acetylide with phenyldiazonium chloride and found that chlorobenzene is formed and acetylene does not take part in the reaction. Sharvina and Plakhuta [95] isolated tetraphenylethane from the products of the reaction of copper acetylide with phenyldiazonium sulphate, showing in this way that acetylene takes part in the reaction to an insignificant extent. Sokol'skii and Nikolenko [96] found that the presence of an electron-withdrawing substituent at the *para*- and especially the *ortho*-positions of the diazonium salt facilitates the entry of the acetylenic radical into the aromatic nucleus:



Robson and Tedder [97,98] first reported the production of compounds containing an azoethynyl grouping. The reaction proceeded thus:



Intermediate products were not isolated.

A new method for the synthesis of azoethynyl compounds by the reaction of aqueous solutions of aryldiazonium chlorides with silver acetylides [99,100] was developed:

$$Ar\overset{+}{N}_2Cl + AgC{\equiv}C{-}Ar' \rightarrow Ar{-}N{=}N{-}C{\equiv}C{-}Ar' + AgCl.$$

All the compounds except one were obtained from diazonium salts containing electron-withdrawing groupings in the *para*- or *ortho*-positions. The simplest compound of this series with two unsaturated phenyl radicals could not be synthesised. 4-Hydroxyazobenzene and bisphenylazophenol were isolated from the products of the reaction of phenyldiazonium chloride with silver phenylacetylide. The competitive formation of phenol with subsequent azocoupling makes the part of the substituents in the nucleus of the diazonium salt understandable.

It is known that the decomposition of diazonium compounds is unimolecular. There are many facts supporting an S_N1 mechanism [101,102]:

$$(Ar{-}\overset{+}{N}{\equiv}N{:})\,\bar{X} \xrightarrow{\text{slow}} Ar^+ + {:}N{\equiv}N{:} + X^-,$$

$$Ar^+ + H_2O \xrightarrow{\text{fast}} Ar{-}\overset{+}{O}H_2 \rightleftarrows ArOH + H^+.$$

$-M$- and $-I$-groupings in the *ortho*- and *para*-positions should hinder the removal of nitrogen (by impeding the displacement of the electrons $Ar{-}\overset{\curvearrowright}{N}{}^+{=}N$) but $+M$- and $+I$-groups should facilitate it. At the azo-coupling stage the substituent will exert an opposite influence on the components.

In the diazonium ion substituents which increase the positive charge on account of an inductive or mesomeric effect will increase its reactivity in relation to aromatic compounds, but $+I$- and $+M$-substituents will decrease it [59]. In the phenol being formed, on the other hand, $-I$- and $-M$-groups, by withdrawing electrons from the aromatic ring, reduce its basicity, and consequently its capability for azo-coupling. Hence the rate of decomposition of the diazonium salts with electron-withdrawing substituents and the tendency to coupling with the phenols being formed will be reduced. At the same time the rate of electrophilic replacement of silver should increase with increase in the electrophilic nature of the diazonium ion. Azoethynyl

compounds can also be obtained from diazonium salts with electron-donating substituents in the nucleus. However, as the example of tolyldiazonium chloride showed, the yields here are very small.

The known similarity of copper and silver acetylides with sparingly soluble salts suggests the possibility of their existing in aqueous medium in equilibrium with the solid a definite concentration of acetylide ions and metal ions:

$$L = [R{-}C{\equiv}C^-][Ag^+]$$

where L is the solubility product. Reaction with diazonium salts could then proceed as a simple exchange:

$$Ag^+ + R{-}C{\equiv}C^- + R'{-}\overset{+}{N}_2 \rightleftarrows R{-}C{\equiv}C{-}N{=}N{-}R' + Ag^+ .$$

The factor displacing the equilibrium to the right is the formation of the C–N covalent bond.

One of the significant objections against this mechanism is the weakness of the acid properties of acetylene and its homologues. The acetylide ions would be completely hydrolysed under the reaction conditions (weakly acid medium):

$$R{-}C{\equiv}C^- + H^+ \rightarrow R{-}C{\equiv}CH .$$

Interaction would lead to a combination of the diazonium salt with acetylene, which, as shown by the example of phenylacetylene[103], proceeds as follows:

$$C_6H_5{-}C{\equiv}CH + Ar\overset{+}{N}_2 \rightarrow (C_6H_5{-}\overset{+}{C}{=}CH{-}N{=}N{-}Ar) \xrightarrow{H_2O}$$

$$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CH{=}N{-}NH{-}Ar \rightleftarrows C_6H_5{-}\underset{\underset{OH}{|}}{C}{=}CH{-}N{=}N{-}Ar .$$

It is also difficult to explain the dependence of the results of the reaction for a single acetylide on the electrophilic nature of the diazonium ion.

The reaction of silver acetylides with diazonium salts can evidently be regarded as an electrophilic substitution similar to the reactions of diazonium fluoroborate with organozinc and organomagnesium compounds[104,105]:

$$R{-}ZnCl + \overset{+}{N}_2{-}Ar \rightarrow R{-}N{=}N{-}Ar + Zn^{2+} + Cl^- .$$

The presence in the reacting molecule of an acetylenic group does not rule out the possibility of yet another reaction mechanism—two-stage addition–splitting. The carbonium ion produced would differ from that obtained from phenylacetylene by the presence of a =C–Ag bond of comparatively low stability. The elimination of the Ag^+ ion in this instance would also lead to an azoethynyl compound.

$$R{-}C{\equiv}CAg + N{\equiv}\overset{+}{N}{-}R \rightarrow [R{-}\underset{\underset{Ag}{|}}{\overset{+}{C}}{=}C{-}N{=}N{-}R'] \xrightarrow{-Ag^+} R{-}C{\equiv}C{-}N{=}N{-}R'$$

However, such a mechanism seems to us much more probable for the following reasons.

It is known[106] that styrylsilver $Ag{-}CH{=}CH{-}C_6H_5$ is insoluble, brightly coloured, and—unlike the alkylethynyl derivatives of silver, for example, $Ag{-}CH{=}C(CH_3)_2$ [107]—is a rather stable compound, stable in air at room temperature for several hours. A comparatively high stability could also be expected from the product of the addition of a diazonium salt to silver phenylacetylide, similar in structure to styrylsilver. Furthermore, in all the examples investigated[106,108] compounds with an Ag–C bond decompose homolytically with liberation of metallic silver.

7. Interaction of Copper Acetylides with Inorganic Compounds

The interaction of $HgCl_2$, $HgBr_2$, and $Hg(OOCCH_3)_2$ with various acetylides has been studied in tetrahydrofuran, dioxan, alcohol, and water[109]. The formation of insoluble compounds was always observed. With an aqueous solution of ammonia the compound decomposes with separation of bisacetylene derivatives of mercury.

An investigation of the product of the reaction of two moles of copper phenylacetylide with one mole of mercury(II) bromide showed that it has the composition $HgBr_2 \cdot 2C_6H_5C{\equiv}CCu$. The complex is insoluble in ordinary organic solvents, soluble in pyridine but in dissolving it decomposes (as under the action of ammonia) into bis-(phenylethynyl)mercury and copper halide. An aqueous alcoholic solution of potassium iodide also decomposes the complex on heating, with liberation of the initial copper acetylide:

$$K_2(HgX_2I_2) + 2\,CuC{\equiv}CR \xleftarrow{2KI} HgX_2 \cdot 2\,CuC{\equiv}CR \xrightarrow{NH_3} Hg(C{\equiv}CR)_2 + 2[Cu(NH_3)_n] + 2\,X^- .$$

It is extremely probable that the reaction of HgX_2 with $R{-}C{\equiv}CCu$ takes place in the coordination sphere of the metals in the solid phase, however, it is also possible to postulate the existence of a double equilibrium between the solid and the solution:

$$HgX_2 + 2\,CuC{\equiv}CR \rightleftarrows HgX_2 \cdot 2\,CuC{\equiv}CR \rightleftarrows Hg(C{\equiv}CR)_2 + 2\,CuX .$$

Potassium iodide can shift the equilibrium only to the side of the formation of the acetylide. Both directions are possible for ammonia in principle, and the result will be determined by the ratio of the reaction rates.

In the infrared spectrum of the complex there are two bands in the range of the stretching vibrations of the triple bond: a weak one at 2000 cm^{-1} and a medium at 2040 cm^{-1}, which evidently shows the presence in the complex of triple bonds of different type. The decrease in the frequencies of the triple bonds compared with the monomeric bis-(phenylethynyl)mercury ($\nu_{C{\equiv}C}$ = 2143 cm^{-1}) suggests their interaction with the copper atoms, but less strongly than in copper phenylacetylide ($\nu_{C{\equiv}C}$ = 1930 cm^{-1}). The position of the bands of the stretching vibrations of the triple bonds and their relative intensities are reminiscent of the same parameters of the infrared spectra described by Coates and Parkin[30] for the tetrameric complex of copper phenylacetylide with trimethylphosphine.

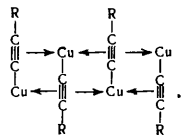
The absence of interaction between bis-(*C*-methylbarenyl)mercury and copper phenylacetylide[109] suggests that a significant part in the formation of such complexes is played by the difference in electronegativity associated with the mercury halide and the ethynyl group of the acetylide. The capability of the more electronegative ethynyl group to withdraw part of the electron density of the readily polarisable mercury atom can lead to the formation of a four-centre structure with bridging halogen atom:

$$\begin{array}{l} Br{-}Hg{-}Br \\ \quad\vdots\quad\vdots \\ R{-}C{\equiv}C{-}Cu \end{array} .$$

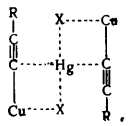
With bis-(*C*-methylbarenyl)mercury the formation of such a cyclic structure is also impossible because of the (already unusually high) coordination saturation of the barene carbon atom, which here should increase the coordination number from six to seven.

The formation of the complex $HgBr_2 \cdot 2CuC{\equiv}CR$, even in the presence of 100% excess of a mercury salt, can be explained by first assuming that oligomeric fragments of

acetylene are constructed from molecules oriented "head to tail":



On p. 1760 a structure was given for the complex $[CuC{\equiv}C\text{-}Ph.PMe_3]_4$, in which the phenyl rings of the acetylide were directed to opposite sides. The same orientation is proposed for the dimeric complexes of the copper[30] and silver[31] acetylides. It has also been suggested[31] that in the copper acetylides every metal atom is π-bonded with not less than two acetylene groupings, resulting in the coordination saturation of these compounds. Hence the structure given above for the mercury complex (not necessarily planar)—is one of the possible variants corresponding to these ideas. In this orientation in the blocks of the acetylide each molecule of the mercury halide can be inserted in the ready "matrix" of two molecules of acetylide:



If the complex is constructed from such fragments linked to one another by the coordination of the π-electrons of the triple bonds with the copper atoms, then even for the dimer an explanation is found for the two bands of the stretching vibrations of the triple bond in its infrared spectrum.

Like mercury, thallium forms two extremely stable covalent bonds with organic radicals. Grignard reagents alkylate thallium(III) chloride to stable and sparingly soluble dialkylthallium chlorides[110]:

$$TlCl_3 + 2\,RMgX \rightarrow R_2TlCl + 2\,MgXCl.$$

The significant difference of the Tl^{3+} salts from the Hg^{2+} salts is the tendency to the formation of ions with an electron cloud containing an "inert pair" determining the strong oxidising properties of the thallium(III) compounds. From the value of the oxidation potential of Tl^{3+} in the reaction $Tl^{3+} + 2e \rightarrow Tl^{+}$ (1.25 $E°$, V), clearly the Tl^{3+} ion occupies a position intermediate between bromine and chlorine (+1.066 and 1.358 $E°$, V respectively).

This feature of the thallium(III) salts was also determining in the reaction between $TlCl_3.4H_2O$ and copper phenylacetylide. The reaction can be represented by the following equation:

$$TlCl_3 \cdot 4\,H_2O + 2\,CuC{\equiv}C{-}C_6H_5 \rightarrow TlCl + 2\,CuCl + C_6H_5C{\equiv}C{-}C{\equiv}C{-}C_6H_5 + 4\,H_2O.$$

Dry copper phenylacetylide in a medium of phosphorus trichloride forms a colourless insoluble complex. An aqueous solution of ammonia or pyridine destroys the complex with the liberation of tri(phenylethynyl)phosphine $(C_6H_5C{\equiv}C)_3P$.

The same course for the reaction is evidently determined by the structure of the reactants, which permits intermediate coordination of one molecule of phosphorus trichloride with three molecules of the acetylide. The zig-zag arrangement of the copper atoms in the oligomeric blocks of the acetylide should facilitate such interaction, bearing in mind the pyramidal structure of the PCl_3 molecule.

It is also known that in many instances an increase in the polarity of the element–halogen bond hinders alkynylation[111]. As the phenylethynyl group is a stronger acceptor of electrons than chlorine its introduction into the molecule should decrease the polarity of the remaining P–Cl bonds and facilitate the subsequent stage of alkylation.

8. Oxidative Condensation of Copper Acetylides

The reactions most widely employed in synthetic organic chemistry are those connected with the oxidation of acetylenic derivatives of copper(I), and above all there is the oxidative condensation of copper acetylides into diacetylene derivatives, discovered by Glaser[112]:

$$2\,R{-}C{\equiv}CCu \xrightarrow{\text{oxidant}} R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

The extensive reviews of the reactions for oxidative condensation of acetylides which have recently appeared[70, 113-115] allow the present discussion to be restricted to only a brief statement of the main stages in the development of this branch of synthesis.

Perhaps the most important changes introduced into the method since the time of the discovery of the reactions was its conversion from heterogeneous to homogeneous. The choice of the conditions under which all the components of the reaction mixture are present in the dissolved state allowed the yields to be greatly increased, the temperature to be decreased, the reaction time to be curtailed and the range of acetylenes employed in the condensation to be greatly extended. Various macrocyclic compounds with diacetylene groupings were obtained from bisacetylenes in extremely dilute solutions for the first time. Methods of oxidative condensation in a homogeneous medium proposed by Hay[116] and Eglinton[117,118] were used most extensively. In Hay's method the reaction is carried out in pyridine with a catalytic amount of copper(I) chloride, using oxygen as the oxidant. In Eglinton's method the solvent is a mixture of pyridine and methanol, and the oxidant copper(II) acetate.

Another significant contribution in the study of the oxidation reactions was Zal'kind and Fundyler's discovery[119,120] of the possibility of carrying out oxidative condensation of acetylenes in an acid medium.

The development of the ideas about the mechanism of the oxidative condensation of acetylenes received detailed discussion in reviews[70,115], which allows the consideration in the present review to be restricted to only the most interesting studies of the principal aspects of these concepts.

The first ideas about the mechanism of oxidative condensation were purely hypothetical. Thus Zal'kind and Fundyler[119,120] suggested that the process starts with the decomposition of acetylenic compound into radicals, which recombine to form a diacetylene derivative:

$$R{-}C{\equiv}CH \rightarrow R{-}C{\equiv}C^{\cdot} + H^{\cdot},$$
$$2\,R{-}C{\equiv}C^{\cdot} \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

The authors advanced the hypothesis that the formation of derivatives of diacetylene is facilitated by an increase in the positive induction effect of the group or atom situated close to the triple bond. The hydrogen liberated is either used up in the hydrogenation of part of the acetylene or is oxidised by atmospheric oxygen to water. The part played by the copper salts and oxygen remains unexplained in Zal'kind's scheme.

Westcott and Baxendale[121] showed that Cu^{2+} ions are oxidants. Thus with a stoichiometric amount of $CuSO_4$ in

an aqueous buffer solution (pH 6) dimethylethynylcarbinol rapidly forms a diyne in 50% yield. The other half of the ethynyl compound is precipitated as copper(I) acetylide:

$$4\,RC{\equiv}CH + Cu^{2+} \rightarrow R[C{\equiv}C]_2R + 2\,RC{\equiv}CCu + 4H^+ .$$

Klebanskii and coworkers[122] proposed a three-stage mechanism for the formation of the diyne in aqueous solution:

$$\text{(I)}\ RC{\equiv}CH \rightleftarrows RC{\equiv}C^- + H^+ \ \text{(slow)},$$
$$\text{(II)}\ RC{\equiv}C^- + Cu^{2+} \rightarrow RC{\equiv}C^{\cdot} + Cu^+ \ \text{(rapid)},$$
$$\text{(III)}\ 2\,RC{\equiv}C^{\cdot} \rightarrow RC{\equiv}C{-}C{\equiv}CR \ \text{(rapid)}.$$

The authors consider that in an alkaline medium the acetylene slowly dissociates with formation of the acetylide ion, which is then oxidised by the Cu^{2+} ion into a radical. The Cu^+ ions do not affect the process. An analogous mechanism is also proposed for condensation in an acid medium but it is suggested that ionisation (1) takes place through the formation of an intermediate complex of type

$$RC{\equiv}C\cdot CuCl\cdot NH_4Cl,$$

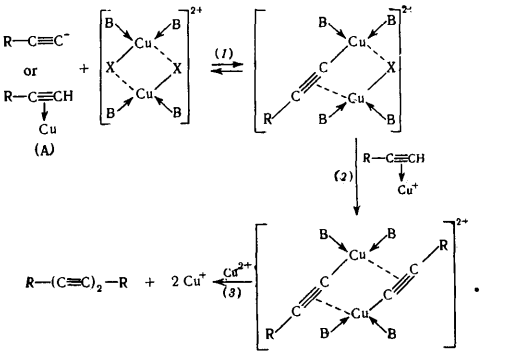
since on introducing an acetylenic compound into weakly acid (pH 4) solution of $CuCl_2$ and NH_4Cl the pH of the medium rapidly drops to pH 1.

Bohlmann and coworkers[123] found that the Klebanskii scheme does not correspond with the experimental results. Were the dissociation determining the rate of reaction to take place by Eqn. (1) the reaction rate would be first order. However, the reaction was always second order. To investigate the kinetics of the reaction, Bohlmann used a solution of the complex of copper(I) chloride with ethanolammonium chloride in 80% aqueous methanol. All the acetylenic compounds and copper(II) chloride are sufficiently soluble in this medium. The Cu^+ and Cu^{2+} are used in large excess. It was shown, by more than ten examples, that the reaction is second order. At pH 3 the reaction rate decreases with increase in the number of conjugated triple bonds. Thus the dimersiation time for half the initial quantity of phenylacetylene is 260 min, for phenyldiacetylene 6900 min, and for phenyltriacetylene 30 000 min. It is remarkable that in alkaline medium the reverse relation is observed (phenylacetylene 35 000 min, phenyldiacetylene 65 min). In pyridine solution the reaction rate increases with increase in the mobility of the acetylenic hydrogen; in acid medium the reverse is observed. In alkaline media the accelerating effect of Cu^+ ions is strongly expressed. The dependence of the reaction rate on the Cu^+ ion concentration is especially evident in the reactions of alkynes with increased mobility of the hydrogen. Thus on varying the concentration of Cu^+ ions from 0 to 100 the rate of dimerisation of the phenylacetylene increases 700 times and that of methyldiacetylene by about twice. The only probable explanation for the action of Cu^+ ions is the formation of π-complexes of the copper with the triple bond. This reaction can be regarded as a quasi-electrophilic addition. In this instance it is clear that with increase in the number of conjugated triple bonds the ability to form π-complexes should fall. The precise structure of these complexes is unknown but it can be assumed that the formation of a π-complex will be facilitated by an increase in the mobility of the acetylenic hydrogen to such an extent that even in acid media the dissociation:

$$R{-}C{\equiv}C{-}H \rightleftarrows R{-}C{\equiv}C^- + H^+$$
$$\downarrow\ Cu \qquad\qquad \downarrow\ Cu^+$$

can proceed.

Cu^{2+} ions take part in Bohlmann's scheme as an oxidant. Since a second-order reaction is observed at a large excess of Cu^{2+} ions the author suggests that the complex is formed from two molecules of the acetylenic compound. The general scheme of reaction can then be expressed in the following way:



In an acid medium copper(I) acetylide can be formed only as a π-complex (A), which then reacts according to (*1*). Thanks to the increase in the acidity of complex (A) and also the increase in the Cu^{2+} concentration, the reaction will be shifted to the right, to the side of the formation of a diacetylenic derivative.

If the reaction is carried out with compounds which contain two terminal acetylenic groups separated by a flexible chain, sufficiently long for ring closure, then the reaction is first order, since stage (*1*) is then an intramolecular reaction. Subsequent confirmation of Bohlmann's scheme was provided by the formation of products of mixed oxidative dimerisation. On assuming the radical nature of the process, the acetylenic radical formed initially should react with the second acetylenic radical selectively. However, it appeared that in the reaction of phenylacetylene with pentenynol in pyridine solution only 0.3% of the mixed dimerisation product is formed, which corresponds with a significantly greater reactivity of the phenylacetylene by the proposed mechanism. The yield of unsymmetrical products of the dimerisation is greater from acetylenic compounds with comparable reactivity.

The oxidative dimerisation mechanism proposed by Bohlmann reflects most completely the reaction process. However, much remains uncertain in this scheme. Thus, no explanation has been found for the reaction rate in alkaline media depending considerably on the amine concentration. The problem of the necessity for the reaction of a Cu^{2+} complex with an amine of definite composition remains open, since the complex is formed only when there is a large excess of amine. The nature of the amine plays a large part in the formation of the complex. Hay[116] showed that a high rate of reaction could be secured by using a total of 5–10 parts tetramethylenediamine per part of Cu^{2+} instead of a large excess of pyridine (as medium). The rate of dimerisation of phenylacetylene under strictly equal conditions varied in the ratio 40 : 7 : 1 on going from pyridine to 2-picoline to 2,6-lutidine.

Interesting results are given in a review[70] with reference to the private communication of Brandt, who found that the reaction of copper ions with acetylene can take place according to the scheme:

$$RC{\equiv}CH + Cu^+ \rightarrow RC{\equiv}CCu + H^+ \ \text{(fast)},$$
$$RC{\equiv}CCu + Cu^{2+} \rightarrow RC{\equiv}CCu^+ + Cu^+ \ \text{(slow)},$$
$$RC{\equiv}CCu^+ \rightarrow RC{\equiv}C^{\cdot} + Cu^+ \ \text{(fast)}.$$

An analysis of the results on the oxidative condensation of acetylenic compounds creates an impression of the possible existence of three different mechanisms for dimerisation in an alkaline medium, leading to a similar result: the oxidation of the acetylide ion, the oxidation of copper(I) acetylide, and finally the formation of an unstable acetylide derivative of copper(II), which decomposes into the acetylene radical and a copper(I) salt.

An example of the realisation of the first mechanism in a pure form is the oxidation of sodium phenylacetylide by permanganate in liquid ammonia[70]; diphenylbutadiene was obtained in 67% yield.

The possibility of the second path scarcely needs proof, since the lengthy time of the Glaser reaction carried out both oxidation of the copper acetylides previously liberated. Copper(II) can also be used as a strong oxidant:

$$R{-}C{\equiv}C{-}Cu + Cu^{2+} \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R + Cu^{+}.$$

Evidently the part of copper(II) here differs significantly from its role in the scheme proposed by Bohlmann, who suggests the formation of an intermediate acetylene complex of Cu^{2+} directly from a copper(II) compound. In the last stage (*3*) of the Bohlmann scheme copper(II) is introduced as an oxidant but this is evidently not necessary since the complex which is formed decomposes spontaneously with homolytic breaking of the transition metal (Cu^{2+})–carbon bond, owing to the instability of this bond.

The work of Coates and coworkers[30-33] also suggests that the copper(I) acetylides themselves already have a structure convenient for dimerisation. It is not difficult to see, for example, that the oxidation of the metal in the phosphinic complex of the acetylide (see p. 1759) leads to a compound analogous to the complex (B) in Bohlmann's scheme.

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On comparing the available information on the stability of the organic compounds of copper and silver with the acetylides of these metals, the following series can be compiled:

$$R{-}M \ll Ar{-}M < Ar{-}\overset{R}{\overset{|}{C}}{=}CH{-}M < R{-}C{\equiv}C{-}M < Ar{-}C{\equiv}C{-}M,$$

where R = alkyl, Ar = aryl, M = Cu or Ag.

Evidently the increase in the stability of the C–M bond in this series is explained, on the one hand, by the stability of the organic radical connected to the metal, and on the other, with the possibility of the formation of polymeric π-complexes. It is well known[124], for example, that phenylcopper is an insoluble polymeric substance. It can be suggested that the relative stabilisation of the C–Cu bond is attained here owing to the formation of Cu–Ph acceptor–donor bonds. In styryl (vinyl) compounds of Cu and Ag the possibility of complex formation is increased owing to the presence of mobile π-electrons of the double bond. Naturally the maximal stability is observed in acetylides.

On comparing the chemical reactivity of aryl derivatives and copper acetylides, clearly the Ar–Cu bond is considerably more active. Thus phenylcopper reacts with benzaldehyde[125], and acetophenone was obtained (54% yield) with acetyl chloride[125]. Information about such reactions with copper acetylides is not available. It should be noted that in addition to ketones a considerable amount of biphenyl is always formed in this reaction. Biphenyl was obtained exclusively in an attempt to condense carbon monoxide with phenylcopper[126].

Phenylcopper reacts with allyl bromide[125], forming allylbenzene in 31% yield. Copper acetylides undergo similar reactions but the yields are then usually higher.

The similarity of the copper acetylides to the organic compounds of copper also appears in the ability of the latter to form complexes with phosphines[127]. Thus, σ-cyclopentadienylcopper forms a stable complex with triethylphosphine $C_5H_5Cu.P(C_2H_5)_3$.

From the above examples it is evidently sufficiently clear that the acetylides of the metals of Group 1b, although exhibiting specific properties, also are closely connected with the organic compounds of these elements.

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Dipole Moments and the Structure of π-Complexes of Metals

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Information on the dipole moments of π-complexes of metals is surveyed and systematised in this article: cyclopentadienyl, arene, alkene, carbonyl, and polymetallic complexes. The possibility of using the dipole moments method for finding the geometric structure of the π-complex molecules, the spatial position of the ligands, and the nature and polarity of the bonds which arise in complex formation has been shown. The results obtained in measurements of dipole moments are compared with data from infrared and NMR spectra, X-ray diffraction, and the chemical properties of the π-complexes. There is a bibliography of 298 references.

CONTENTS

I.	Introduction	763
II.	Cyclopentadienyl, arene, and cycloalkene complexes of the transition metals	764
III.	Carbonyls and nitrosyls of metals	766
IV.	Complexes of metal salts with unsaturated hydrocarbons	773
V.	Complexes of the halides of the elements of Groups III–V with aromatic hydrocarbons	774
VI.	Polymetallic $\pi\sigma$-complexes	775

I. INTRODUCTION

There is now an ever-increasing interest in the study of the structure of coordination compounds, in which the bond of the metal with the ligand is delocalised and brought about by interaction of the molecular π-orbitals of the ligand with the corresponding orbitals of the metal.

A series of monographs[1-4] and reviews[5-12] have generalised and systematised the information on the properties and structure of the π-complexes; these publications consider the results obtained by the methods of vibrational and NMR spectra, magnetochemistry, X-ray diffraction, and electron diffraction.

However, in none of these, nor in any of the other monographs[13-15] of a more general nature, is sufficient attention paid to the results of investigations of the polar properties of the π-complex molecules. Nevertheless a considerable number of papers has now been published[16-17] on the study of the structure and properties of coordination compounds by the dipole moment method, which gives valuable information on the geometrical structure of the molecules of the complexes, the spatial position of the ligands, the nature and polarity of the bonds arising in complex formation.

Interpretation of the values of the dipole moments does not require complicated mathematical equipment needed for dealing with the results from several other methods. However, it should be noted that the dipole moments method and vector calculations cannot always give an unambiguous characterisation of the structure of a complex molecule containing several polar groups. Because of this a knowledge of the value of the dipole moment is especially convenient when it is necessary to find which of several probable structures (*cis*- or *trans*-, centrosymmetric or otherwise) truly corresponds with the physical and chemical properties of the complex. The results obtainable on measuring the dipole moments are of special interest and cannot be replaced by X-ray structural investigations, since unlike the latter they characterise the structure of individual molecules in solution and not in a condensed phase.

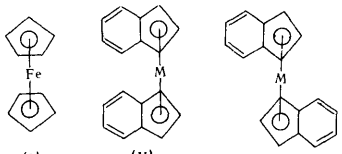
The present review surveys material (up to 1968) on the study of polar properties and the structure of coordination compounds of the transition metals and the halides of the elements of Groups III–V with unsaturated and aromatic and nitrosyl complexes. We usually compare the conclusions nitrosyl complexes. We usually compare the conclusions drawn from the values of the dipole moments with the results of other methods of investigation (infrared and NMR spectroscopy, X-ray diffraction, etc.) and also from certain data on the chemistry of the π-complexes.

The methods of determining dipole moments and the problem of estimating and calculating atomic polarisation are not examined in this review as these problems were discussed earlier[16,18-24].

II. CYCLOPENTADIENYL, ARENE, AND CYCLOALKENE COMPLEXES OF THE TRANSITION METALS

1. Cyclopentadienyls and Cyclopentadienides

Even in the first paper[25] devoted to the study of the structure of biscyclopentadienyliron, synthesised by Kealy and Pauson[26], on the basis of the zero value of the dipole moment and the results of other methods of investigation the now generally accepted structure (I) was proposed for ferrocene†:



M = Fe, Ru.

(I) (II) (III)

The zero value of the dipole moment was subsequently used as an unambiguous criterion of the high symmetry and sandwich structure of various cyclopentadienyl complexes of transition metals (Table 1).

Of the data given in Table 1,[25,28-42] attention may be paid to the different values of the atomic polarisation (P_A) at which the values of the dipole moments of the complexes reach zero. Taking into account that the ratio $(P_A + P_E)/P_E$ ‡ is a unique criterion of the "ionicity" of the bonds in the complexes[43], conclusions can be drawn about the largest ionicity of the cyclopentadienyl derivative of magnesium. This conclusion is also confirmed by the results of an investigation of magnesium biscyclopentadienide by mass spectroscopic and X-ray diffraction methods[6].

The different nature of the bond in cyclopentadienyl complexes can be observed not only from the values of P_A, but also from the changes in the values of the dipole moments of the complexes in different solvents[32]. Whereas in *cyclopentadienyls* with a pure covalent bond and low values of P_A (ferrocene, nickelocene, etc.) the dipole moment hardly changes on going from heptane to dioxan, for the "ionic" magnesium and manganese cyclopentadienyls it increases by 1.9 and 2.3 D respectively[32].

In addition to the *dipole-free* cyclopentadienyl complexes there is a group of compounds with a dipole moment different from zero: these are the derivatives of beryllium, tin, bismuth, lead[29,31], manganese[32], mercury[34], and also tantalum, niobium[38], molybdenum[39], and lutetium[36]. The explanations for the polarity of these derivatives are contradictory. Whereas in the early studies[29] suggestions are advanced concerning the organometallic nature of these complexes with an angled position for the σ-bound rings, it was subsequently shown that the $Pb(C_5H_5)_2$ and $Sn(C_5H_5)_2$ molecules are "sandwich" with non-parallel cyclopentadienyl rings[6,31,34,42,44]. An investigation of the structure of the metal biscyclopentadienyls using gas electron diffraction leads to the same conclusion[8,11].

Nevertheless, on the basis of the infrared and NMR spectra Fritz[44,45] does not rule out the possibility of σ-bonding of one of the five-membered rings in $Pb(C_5H_5)_2$ and $Pb(C_5H_4CH_3)_2$.

We see[46] that the cyclopentadienyl rings are also non-parallel in the $Zn(C_5H_5)_2$ molecule. Moreover, an angular arrangement of the σ-bound nuclei has been demonstrated[47] for $Hg(C_5H_5)_2$ with dipole moment 1 D.[34]

† The electronic structure of ferrocene has been discussed by Shustorovich and Dyatkina[27] and also by several other foreign authors[4].

‡ P_E is the electron polarisation.

The dipole moment (~ 2.5 D) of $Be(C_5H_5)_2$ was at first attributed to the presence in its molecule of π- and σ-bound cyclopentadienyl rings[31,34,35]. However, an investigation of the structure of biscyclopentadienylberyllium in the gas phase by electron diffraction shows the free motion of the Be ion in the cell formed by the five-membered rings, and explains the value given above for the moment by the possibility of the metal's being situated at a different distance from the π-cyclopentadienyl nuclei[8,48]. The last feature leads to the polar C_{5v} symmetry[48]. An examination of its infrared spectrum shows that $Be(C_5H_5)_2$ also has an asymmetric sandwich structure[49].

Table 1. Dipole moments of the cyclopentadienyl complexes of metals.

Compound	Name *	Solvent **	P_A, % of P_E	Dipole moment μ, D	Reference
$[\pi\text{-}C_5H_5]_2Fe$	bis-(π-cyclopentadienyl)iron(II) (ferrocene)	B	6	0	25, 28
		CCl_4	—	0	29, 30
$[\pi\text{-}C_5H_5]_2Ni$	bis-(π-cyclopentadienyl)nickel(II) (nickelocene)	B	2.5	0±0.33	31
		D		0	
$[\pi\text{-}C_5H_5]_2Co$	bis-(π-cyclopentadienyl)cobalt (cobalticene)	B	5.1	0±0.38	31
$[\pi\text{-}C_5H_5]_2Ru$	bis-(π-cyclopentadienyl)ruthenium (ruthenocene)	B	5.2	0±0.23	31
$[\pi\text{-}C_5H_5]_2Os$	bis-(π-cyclopentadienyl)osmium (osmocene)	B	1.6	0±0.30	31
$[\pi\text{-}C_5H_5]_2V$	bis-(π-cyclopentadienyl)vanadium	B	2.2	0±0.34	31
$[\pi\text{-}C_5H_5]_2Cr$	bis-(π-cyclopentadienyl)chromium (chromocene)	B	15	0±0.41	31
		D		0.6	32
$[C_5H_5]_2Mg$	magnesium cyclopentadienide	B	31	0±0.35	31
		D		2.7	32
$[C_5H_5]_2Mn$	manganese cyclopentadienide	H		1.0	
		B		1.0	32
		D		3.3	
$[C_5H_5]_2Sn$	bis(cyclopentadienyl)tin	B	10	1.09±0.06	29
		H	—	0.9	32
		C	15	0.96±0.1	31
		D	—	1.2	32
		CS_2		1.49±0.06	33
$[C_5H_5]_2Pb$	bis(cyclopentadienyl)lead	B	10	1.63±0.06	29
		D		1.0	34
				2.16	32
		C	15	1.29±0.04	31
		CS_2	10	1.49±0.06	33
$[C_5H_5]_2Be$	bis(cyclopentadienyl)beryllium	C	15	2.24±0.09	32, 35
		B	15	2.46±0.06	31
		D		2.6	32
$[\sigma\text{-}C_5H_5]_2Hg$	bis-(σ-cyclopentadienyl)mercury	B		1.0	34
$[C_5H_5]_3Bi$	tris(cyclopentadienyl)bismuth	B	15	1.17	31
$[C_5H_5]_3Lu$	tris(cyclopentadienyl)ruthenium	B	—	0.86±0.05	36
$[C_5H_5]_4U$	tetrakis(cyclopentadienyl)uranium	B	—	0	37
$[C_5H_5]_4Ta$	tetrakis(cyclopentadienyl)tantalum	B		4.09±0.03	38
$[C_5H_5]_4Mo$	tetrakis(cyclopentadienyl)molybdenum	B	—	2.61±0.15	39
$[\pi\text{-}C_5H_5]_2ReH$	bis-(π-cyclopentadienyl)rhenium hydride	B	15	1.17	31
$[\pi\text{-}C_5H_5]Cr$ $[\pi\text{-}C_7H_7]$	π-cyclopentadienyl-(π-cycloheptatrienyl)-chromium	B		0.79±0.05	40
				0.73±0.05	41
$Co_2C_{25}H_{24}$	2,4-bis(cyclopentadienylcobaltcyclopentadien)yl-cyclopenta-2,4-diene	B		0	29
$[C_5H_5]_3Y$	tris(cyclopentadienyl)yttrium	B		1.46	42

* Given by Wilkinson and Cotton[6].

** B = benzene, D = dioxan, C = cyclohexane, H = heptane.

Similar considerations explain[41] the polarity (μ = 0.8 D)[40,41] of cycloheptatrienyl(cyclopentadienyl)chromium $C_5H_5Cr^0C_7H_7$. Clearly the complex $C_5H_5V^0C_7H_7$,[50] in which according to X-ray diffraction data the metal is found at a different distance from the planes of the cyclopentadienyl (1.9 Å) and cycloheptatrienyl (1.5 Å) rings[51], should also be polar.

The polarity of tetrakis(cyclopentadienyl)tantalum[38] and tetrakis(cyclopentadienyl)molybdenum[39] is explained by the participation in the formation of their molecules of σ- and π-bonded cyclopentadienyl rings, and that of manganese cyclopentadienide by the high "ionicity" of the bonds in this complex[32].

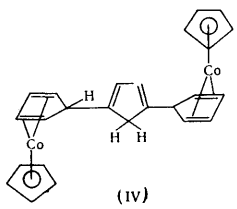
In connection with what has been stated it must be borne in mind that the values of the dipole moments cannot be an unambiguous criterion allowing the π-cyclopentadienyls to be distinguished from the usual organometallic compounds: the zero value of the moment shows the high symmetry of the molecule, but the appearance of polarity is not necessarily due to a change in the nature of the bonding. Therefore the conclusions concerning the type of bonds in the cyclopentadienyl complexes of metals drawn solely on the basis of values of dipole moments must be approached with caution.

The values of the dipole moments have been used to determine the possibility of free rotation of the cyclopentadienyl rings of disubstituted ferrocenes. Richmond and Freiser[52], who determined the dipole moments of the monoacetyl- (3.02 D) and diacetyl- (4.23 D) ferrocenes, concluded there was free rotation of the acetylcyclopentadienyl rings around an axis perpendicular to these nuclei[52]. However, these quantities can also be consistent with a restrained configuration[5].

A similar conclusion is also valid for *p*-chlorophenylferrocene[53]: the value found for its dipole moment (3.12 D) agrees best with those calculated for the 1,1'-prismatic (3.12 D) or antiprismatic (2.97 D) models. The value of the dipole moment calculated assuming free rotation of the *p*-chlorophenylcyclopentadienyl rings is 2.2 D.[53,54]

It is now assumed that whereas for ferrocene itself free rotation is only slightly restricted[3,4,6,55], bulky substituents can significantly inhibit it[54,56,57].

The bis(indenyl) derivatives of iron[31] and ruthenium[29] can be considered to belong to this class of compounds. These are extremely interesting as compounds having different structures in the crystalline state and in solution. The X-ray diffraction results show the asymmetric *cis*-position of the indenyl rings (II) in relation to the metal[58] and the zero value of the dipole moment gives a basis for attributing to the bis(indenyl) compounds the symmetric structure (III) with *trans*-arrangement of the ligands[31]. A study of the NMR spectra of indenyl complexes leads to the same conclusion[59]. The determination of the dipole moments of derivatives of ferrocene[60] and biferrocenyl[61], for which X-ray diffraction studies have been made[62-64] is of considerable interest in this connection.



(IV)

An interesting cyclopentadienyl derivative of a metal is the dinuclear complex $Co_2C_{25}H_{24}$. The structure first proposed for this compound, pentakis-(π-cyclopentadienyl)-dicobalt $(C_5H_5)Co_2$ in which each cobalt atom forms a trigonal prism surrounded by three cyclopentadienyl rings[29], was subsequently disproved[65-69]. It has now been found[69] that the molecule of this complex, which is 2,4-bis-(π-cyclopentadienylcobaltcyclopentadien)ylcyclopenta-2,4-diene, is constructed from two sandwich fragments connected through a planar cyclopentadiene bridging ring (IV). This structure agrees with the low polarity of complex (IV).[29]

2. Arene Complexes

The absence of a dipole moment was an important argument in support of a highly symmetric sandwich structure for bis(benzene)chromium[70] and several of its derivatives[29,31,71]. Just as for ferrocene, the atomic polarisation for the arene complexes of chromium is not more than 5–10% of the electronic polarisation; this has been shown not only by calculation[29] but also by the infrared spectra: P_A for bis(benzene)chromium is 3.3 ± 1 cm³ and that for bis(mesitylene)chromium[72] is 3.2 ± 0.7 cm³. In relation to these compounds the high dipole moments of bis(hexamethylbenzene)cobalt $Co[C_6(CH_3)_6]_2$, 1.78 D[73]—and the analogous chromium derivative (1 D)[74] seem extremely strange. The values given for the moments refute a centrosymmetric structure[73] but the reason for the polarity of these complexes is still not clear§.

This type of compound also includes the arenechromiumcyclopentadienyls[31], which do not have a dipole moment.

Determination of the dipole moment makes it possible to find certain details in the structure of heteroangularly substituted bis(benzene)chromium complexes. Thus the absence of dipole moments shows the *trans*-position of the substituents in the arene nuclei of bis(toluene)- and bis-(xylene)-chromium[31].

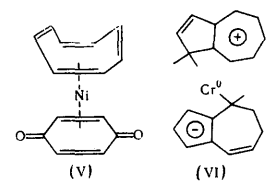
3. Cycloalkene Complexes

A large number of π-complexes of the transition metals with cycloalkenes[76-78], *p*-quinones[79,80], and acyclic alkenes[10,81] is now known.

Unlike the cyclopentadienyl and arene compounds, the cycloalkene complexes of metals are usually polar. Cycloheptatriene(cyclopentadienyl)chromium(0) $C_7H_8CrC_5H_5$ has a dipole moment of 1.1 D,[77] 1,3,5-cyclo-octatriene(cyclopentadienyl)chromium(0) 1.4 D.[77] The low dipole moment of (1.2 D) of π-cycloheptadienyl(cyclopentadienyl)nickel $C_5H_5NiC_5H_7$, which was initially given the structure of bis(cyclopentadienylnickel)[76] in error, agrees well with its unsymmetrical structure.

For the same reason allyl(cyclopentadienyl)palladium (μ = 1.5 D)[82] is polar. Nevertheless among similar complexes compounds with zero dipole moments are encountered, for example, benzene(cyclohexa-1,3-diene)-iron(0).[78]

π-Complexes of nickel with duroquinone and cyclooctatetraene (V), bicyclo[2,2,1]hepta-2,5-diene, bicyclopentadiene, and cyclo-octa-1,5-diene exhibit high dipole moments (3.5–4.3 D), due, evidently, to the high contribution of the polar structures[79,80].



(V) (VI)

It has been found that the value of the dipole moment depends on the polarity of the π-alkene bond and varies symbathically with the donor strength of the alkene ligand[80].

Of the cycloalkene π-complexes the bis(azulene) derivatives of chromium (VI) and iron[83,84] are of considerable

§ Nicholson and Longuet-Higgins[75] explain this anomaly by the Jahn-Teller effect.

interest. The slight polarity (1.18 D) of the chromium complex can scarcely serve as a basis for the structure proposed for it (VI). Here the polar properties are possibly connected with a difference in the distance of the metals from the planes of the azulene rings[8].

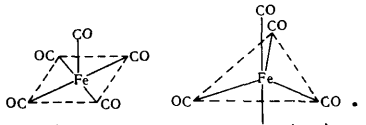
III. CARBONYLS AND NITROSYLS OF METALS

A series of detailed reviews[3,6,10,85,86] have dealt with the nature of the bonds, the methods of preparation, and properties of the carbonyls and the related nitrosyl, isonitrile, and cyano-complexes, but have not, however, considered the polar properties of these compounds.

1. Mononuclear Carbonyls and Nitrosyls

The absence of a dipole moment[87,88] shows the symmetrical nature of the tetracarbonylnickel molecule and can be consistent with planar, square, or tetrahedral configurations. This conclusion is not contradicted by the data obtained in investigating $Ni(CO)_4$ by other physical methods: study of the Raman spectra shows a planar configuration[89], but the infrared spectra[89,91] and electron diffraction[92] allow this complex to be assigned a tetrahedral structure.

The dipole moment for pentacarbonyliron $Fe(CO)_5$, determined by various authors, varies within the range 0–0.8 D. On the basis of the values first obtained for the moment (0.64 [92] and 0.81 D [93]) a square-pyramidal structure (VII) was proposed for $Fe(CO)_5$ and the non-polar configuration of a trigonal pyramid (VIII) was rejected. The non-zero values of the dipole moments were contradicted, however, by the results of an investigation of $Fe(CO)_5$ by vibrational spectroscopy[13,91,94] and by electron diffraction[95], according to which a trigonal bipyramidal structure was proposed for this complex:



(VII) (VIII)

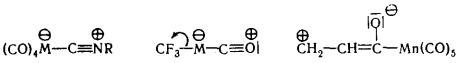
Later investigations made by Weiss[96] showed that on taking account of the atomic polarisation (20% of the electronic) the value of the dipole moment is close to zero. A definitive solution of the problem in support of structure (VIII) gives a zero value to the dipole moment of $Fe(CO)_5$ obtained by a microwave method[97]. This conclusion is confirmed by the similarity in the values found experimentally for the entropy[98] and those calculated from spectroscopic data, and also by the X-ray diffraction results[99,100].

Carbonyls in which CO groups have been replaced by nitrosyl ligands have dipole moments extremely close to zero. Tricarbonylnitrosylcobalt $Co(CO)_3(NO)$ exhibits a moment of 0.4 D ($P_A = 20\% P_E$) and that of dicarbonyldinitrosyliron $Fe(CO)_2(NO)_2$ is 0.7 D.[96]

The low polarity of the carbonylnitrosyls[96], hydrogen pentacarbonylmanganate[101], and alkyl and aryl pentacarbonylmanganates (at an atomic polarisation equal to 20% of the electronic their dipole moment is 0–0.5 D[102,103]) gives a value of 0.5–0.8 D for the moment of the M–Co bond[96,104,105]. Measurements of the dipole moments of the cyclopentadienylcarbonyl complexes lead to the same value¶.

¶ For more details about these complexes, see below.

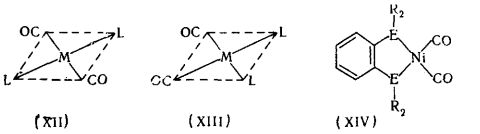
The introduction of polar groups into the complexes leads to a sharp rise in their dipole moments. The moment of $Fe(CO)_4(CNCH_3)$ is 5.07 D.[96] This value cannot be explained by the polarity of the isocyanide with dipole moment 2.5 D [106] and is connected with the high polarisation of the donor–acceptor bond (structure IX).



(IX) (X) (XI)

Analogous polar structures are proposed to explain the dipole moments of the complexes $CF_3Mn(CO)_5$ (X) 3.6 D and $RCOMn(CO)_5$ (R = Alk, 2.3 D; CF_3, 3.5 D; Ar, 2.3 D) and also of acrylic acid derivatives (XI) 2.4 D.[103] Similar dipole moments are possessed by the rhenium carbonyls $CH_3CORe(CO)_5$ 2.5 D and $C_6H_5CORe(CO)_5$ 2.6 D [103] and also the nickel complexes[105,107] $Ni(CO)_3PAr_3$ 3.84 D and $Ni(CO)_3AsAr_3$ 3.59 D.

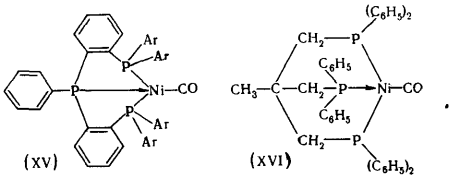
The values of the dipole moments of the planar dicarbonyl complexes of the type $L_2M(CO)_2$ are determined by their stereochemistry: the *trans*-isomers (XII) should not have dipole moments but the *cis*- (XIII) should exhibit considerable polarity:



(XII) (XIII) (XIV)

where E = As or P.

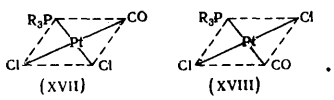
The moment of bis(chlorocarbonyl)platinum is 3.65 D [104] and therefore the complex is ascribed the *cis*-structure (XIII; M = Pt, L = Cl). $Ni(CO)_2(AsAr_3)_2$ with dipole moment 3.34 D and $Ni(CO)_2(PAr_3)_2$ with 3.82 D have the *cis*-configuration[105]†. The *cis*-structure seems the only possibility for complexes (XIV): their dipole moments lie in the range 5–5.5 D.[105,107] Taking into account that the Ni–C–O group is of low polarity (0.5 D) the authors estimate the moments of the Ni–P and Ni–As bonds to be 3.4 and 3.2 D respectively[105]. The same value for the Ni–P bond is also obtained from the value of the dipole moments for the monocarbonylphosphinic complexes (XV, $\mu = 5.18$ D) and (XVI, $\mu = 4.95$ D):[109]



(XV) (XVI)

For the same reason the Fe–P bond should also exhibit considerable polarity, since the dipole moment of $Fe(NO)_2[P(C_6H_5)_3]_2$ is 4.99 D.[110]

Chatt and coworkers investigated the polar properties of monocarbonylphosphinic complexes of platinum(II) chloride[111]. On the basis of the high values of the dipole moments (~ 10 D) and the infrared spectra the *cis*-structure (XVII) is ascribed to these complexes: the *trans*-isomers (XVIII) should have lower moments[111]:



(XVII) (XVIII)

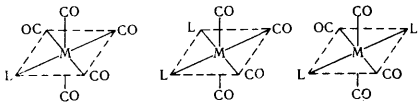
† For $Ni(CO_2)(PEt_3)_2$ of the same structure $\mu = 4.4$ D.[108]

The polar properties of the metal carbonyls and nitrosyls $M(CO)_5L$, $M(CO)_4L_2$, $M(CO)_4L$, $M(CO)_3(NO)L$, $M(CO)_2(NO)L$, and $M(CO)_2L$, where L is a p-electron donor, and M the metal, depend on both the geometry of the molecule and the polarity of the M–L bond.

The high value of the dipole moment is characteristic for the halogenopentacarbonyls of manganese $Mn(CO)_5L$ (for the bromo-derivative μ = 3.2 D [103] or 3.99 D, [112] for the iodo-derivative 3.25 D [103]) and for the derivatives of chromium, molybdenum, and tungsten with nitrogenous bases (L = pyridine, quinoline, piperidine, and aniline 6–7 D [113]). For all these complexes structure (XIX) is assumed and the formula

$$\mu_{M-L} = \mu_{expt} - \mu_{M-Co} - \mu_L$$

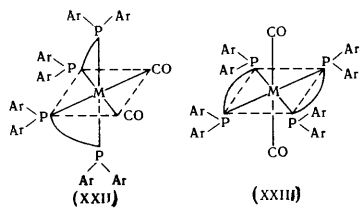
can be used to determine the partial dipole moment of the M–C bond [113]. For $Cr(CO)_5L$ and $Mo(CO)_5L$ the latter lies within the limits 3.6–4.1 D; for $W(CO)_5L$ it is higher by 0.7 D and only depends slightly on the nature of the donor [113]. It is somewhat lower (2.5–3.3 D) only for complexes with acetonitrile, benzonitrile, and aniline [113].



(XIX) (XX) (XXI)

For complexes of the $M(CO)_4L_2$ type *cis*- (XX) and *trans*- (XXI) configurations are possible and the values of the dipole moments can vary from 10 (XX) to 0 (XXI) D. The values of the dipole moments of the *cis*-phosphinic derivatives of the tetracarbonyls of chromium, molybdenum, and tungsten lie within the limits 7–8 D. [114] $Mo(CO)_4$. .2Py has a moment of 9.3 D, the analogous tungsten complex 10.3 D, [113] and $Cr(CO)_4[P(C_6H_5)_3]_2$ and $Cr(CO)_4$.2(cyclohexylnitrile), which have been assigned the *trans*-structure, do not possess dipole moments [115].

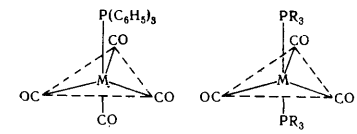
The calculated dipole moment for the *trans*-structure is zero, and that for the *cis*- can be calculated by the formula $\mu_{cis} = \mu_{mono}\sqrt{2}$ (for a regular octahedron), where μ_{mono} is the moment of the complex $M(CO)_5L$ with the same donor, and agrees satisfactorily with the values obtained experimentally [113]. It should be noted that only the *cis*-isomers of the above Mo and W complexes have been isolated, whereas both configurations are known for the chromium compounds [114]. Similar regularities are also observed for the dicarbonyl complexes of the Group VI metals with bidentate phosphines [114]. For $[Cr(CO)_2\{C_2H_4(PAr_2)_2\}_2]$ both the *cis*- (XXII; μ = 6.2 D) and the *trans*- (XXIII; μ = 6.95 D) isomers are known but the similar molybdenum and tungsten complexes with dipole moments 6.15 and 6.7 D respectively, have only the *cis*-octahedral structure (XXII). [114]



(XXII) (XXIII)

The dipole moment of *cis*-$Fe(CO)_4.(HgCH_3)_2$ is extremely low—2.1 D. [116] There may be an equilibrium of the *cis*- and *trans*-isomers in solution here.

The reasons for the considerable differences in the values of the dipole moments of triphenylphosphineirontetracarbonyl $Fe(CO)_4.P(C_6H_5)_3$, 5.1 D [110] and of the analogous manganese derivative $Mn(CO)_4.P(C_6H_5)_3$‡, 1.1 D [117] and mononitrosyltriphenylphosphinemanganesetricarbonyl $Mn(NO)(CO)_3P(C_6H_5)_3$, 4.9 D, [110] to which is assigned a trigonal bipyramidal structure (XXIV): [110,117,118]

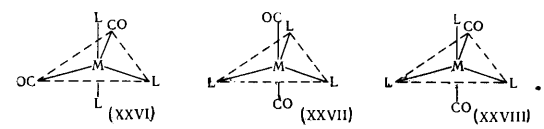


(XXIV) (XXV)

are not understood.

Attempts to explain these differences by the large contribution of the polar form $\bar{M} \leftarrow \overset{+}{P}(C_6H_5)_3$ do not appear to be very convincing in relation to the nitrosyl complex $Mn(NO)(CO)_3.P(C_6H_5)_3$. [110] The anion $[Mn(CO)_4(PAr_3)]^-$ is assigned a trigonal bypyramidal structure on the basis of the identical values of the dipole moments (5.1 D) of $HMn(CO)_4PAr_3$ and $Fe(CO)_4PAr_3$. [119] However, such a comparison can scarcely be considered an unambiguous criterion in the solution of structural problems particularly as the octahedral complex $CH_3Mn(CO)_4PAr_3$ has a moment (4.9 D), extremely close to that given above [119]. Dipole moments close to zero suggest for the complexes $Fe(CO)_3[P(C_6H_5)_3]_2$, [120] $Mn(CO)_2(NO)[P(C_6H_5)_3]_2$, and $Mn(CO)_2(NO)[P(C_6H_{11})_3]_2$ [110] the trigonal bipyramidal model (XXV) with *trans*-PR_3 groups. As Hieber and Tengler [110] consider, the tetragonal pyramidal and trigonal bipyramidal structures with *cis*-arrangement of the PR_3 ligands which are formally possible here should have a dipole moment of ~ 5 D. [110] In this instance it is not clear what structure is characteristic for $Fe(CO)_3[P(OC_6H_5)_3]_2$ with a moment 2.31 D. [121]

The high value of the dipole moment (4.97 D) allows tris(triphenylphosphine)irondicarbonyl to be assigned the structure of a trigonal bipyramid with CO groups lying at the vertices of the triangular base (XXVI). [121] The possible structure (XXVII), is rejected on the basis of the infrared spectra, and (XXVIII) should have a dipole moment of ~ 7 D: [121]



(XXVI) (XXVII) (XXVIII)

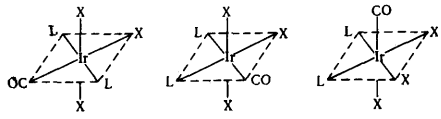
A structure analogous to (XXVI) is proposed starting from the values of the dipole moments and the results of studies of the infrared spectra, for the phosphine derivative of the dicarbonyl halides of cobalt(II) [122] and also for $IMn(NO)_2[P(C_6H_5)_3]_2$ with moment 3.19 D. [123]

For the triphenylphosphinedinitrosyliron halides, $Fe(NO)_2P(C_6H_5)_3X$, it was noted [124] that there is an increase in the dipole moment with increase in the atomic weight of the halogen (X = Cl, μ = 6.78 D; Br, μ = 7.02 D; I, μ = 7.21 D). The same regularity was observed earlier for the analogous complexes of cobalt [125]. However, the increase in the moment in the last instance is insignificant (Cl 6.79 D, Br 6.83 D, I 6.89 D [125]), as it is for the halogen derivatives of pentacarbonylmanganese [103]. More significant changes in the values of μ are characteristic

‡ According to Sidgwick's rule this compound should be a dimer and consequently diamagnetic. However, published data [117] show it to be paramagnetic (1.86 μ_B) and monomeric (M_{exp} = 420; M_{calc} = 429.2).

for the complexes being considered on replacing the phosphorus by other elements of Group V: whereas the dipole moment of $Co(NO)_2P(C_6H_5)_3Br$ is 6.83 D, that for the analogous manganese derivative is 6.4 D and that for antimony 5.26 D.[125] The phosphine-substituted complexes $Co(NO)(PAr_3)_3$ and $Co(NO)(CO)_2PAr_3$ should have similar dipole moments for a tetrahedral configuration. Actually, if the atomic polarisation is not taken into account, then for $Ar = C_6H_5$ the moments of these complexes amount to 4.27 and 4.56 D respectively, and for $Ar = OC_6H_5$ 2.38 and 2.27 D.[125] However, at $P_A = 20\% P_E$ the values of the dipole moments in the first instance differ by 1.2 D, but in the second, by 0.5 D.[125] The reasons for these differences are, in the opinion of these authors[125], connected with the distortion of the valence angle of the tetrahedron under the influence of the bulky PAr_3 groups.

On the basis of dipole moments the configuration of the isomeric carbonyl complexes of the type $IrX_3(CO)(ER_3)_2$, where X = Cl, Br; E = P, As, Sb, and R = Alk, Ar, and of the iridium carbonyl hydride $IrHCl_2(CO)[P(C_2H_5)_2C_6H_5]_2$ was established[126]. For these complexes with X = Cl, E = P, and R = C_2H_5, two, (XXIX) and (XXX), of the three possible isomers, (XXIX)–(XXXI), were isolated and all three of the analogous butyl derivatives: (XXIX) 2.35 D, (XXX) 9.55 D, (XXXI) 12.35 D.[126]



(XXIX) (XXX) (XXXI)

Two isomers, (XXIX) and (XXX), are observed for the phosphinic complex $IrCl_3CO[P(C_2H_5)_2(C_6H_5)]_2$ with dipole moments 3.3 and 9.65 D, for the analogous arsenic derivatives 2.95 and 9.8 D, and also the carbonyl hydrides $IrHCl_2(CO)[P(C_2H_5)_2(C_6H_5)]_2$ 1.2 and 5.1 D.[126] The complexes $IrBr_3(CO)[P(C_2H_5)_2(C_6H_5)]_2$ and $IrCl_3(CO)[Sb(C_3H_7)_3]_2$ are assigned the configuration (XXIX) (their dipole moments are 3.4 and 2.4 D respectively), but $IrCl_3(CO)[As(C_2H_5)_3]_2$ with moment 9.65 D and the bromo-derivative of the above carbonyl hydride (5.35 D) the configuration (XXX).[126]

From the dipole moments (2.5–3.5 D) the *trans*-structure can be assigned to complexes of the general formula $Rh[(XC_6H_4)_3M]_2(CO)Cl$, where M = P, As, and X = H, CH_3, Cl, OCH_3.[127]

Analogous results were obtained for the carbonyl-phosphinic derivatives of rhenium and manganese[120,128]. For $Re(CO)_3[P(C_6H_5)_3]_2I$ *cis*- and *trans*-isomers were observed[128] with dipole moments of 7.6 and 3.0 D respectively but for $Re(CO_3)[P(OC_6H_5)_3]_2I$ only the *cis*-isomer (5.7 D). The carbonyl hydride derivatives of manganese $HMn(CO)_3[[(C_6H_5)_3]_2$ with dipole moment 0.58 D and $HMn(CO)_3.[P(OC_6H_5)_3]_2$ with 2.09 D[120] analogous to the rhenium complex $HRe(CO)_3.[P(C_6H_5)_3]_2$ with 2.5 D,[128] and also carbethoxybis(triphenylphosphine)tricarbonylmanganese (1.7 D),[129] have the *trans*-structure. In this connection the dipole moment of the recently synthesised[130] *cis*-isomer $HMn(CO)_3.[P(OC_6H_5)_3]_2$ is of definite interest.

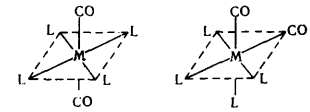
The dipole moment values allow the isomers of halogenophosphinic derivatives of manganese carbonyls to be distinguished[112]. The complex $Mn(CO)_3[P(OC_6H_5)_3]_2Br$ with dipole moment 4.78 D is ascribed the *cis*- and the compound with $\mu = 3.52$ D the *trans*-structure[112].

$$Re(CO)_3[(C_6H_5)_3PO]_2X$$

(X = Cl, Br, I; μ = 8–10 D) has the *cis*-structure[131].

Similar conclusions concerning the structure of complexes of the $L_3MN(CO)_3X$ type follow from their infrared spectra[130,131].

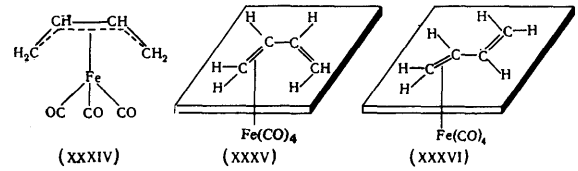
Structural problems similar to those described above also arise in solving problems of the configuration of complexes of type $M(CO)_2L_4$.[132] Here, in addition to an isomer without a dipole moment (XXXII) with *trans*-arrangement of the CO groups (D_{4d} symmetry), a polar *cis*-form should exist (XXXIII, C_{2v}).



(XXXII) (XXXIII)

2. Diene- and Polyene-carbonyls

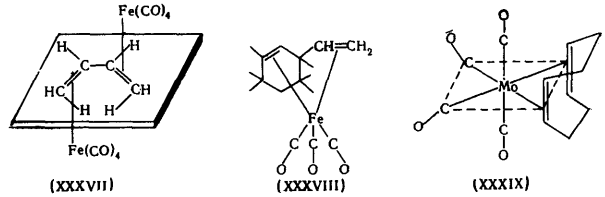
The simplest complexes of this type are the butadieneirontri- and tetracarbonyls[133–136]. Undoubtedly these compounds are of the π-complex type[10,136]. Hallam and Pauson[134] proposed structure (XXXIV) for butadieneirontricarbonyl, and this was confirmed[10,137] by X-ray structural data[138] and chemical properties. The infrared spectrum of butadieneiron tetracarbonyl shows that complex formation takes place through only one π-bond[135].



(XXXIV) (XXXV) (XXXVI)

It seems probable that there are two structures with *cis*- (XXXV) or *trans*- (XXXVI) arrangement of the butadiene fragment (analogous structures can also be postulated for butadieneirontetracarbonyl). The dipole moment method was used to distinguish these structures[135]. However, the values of the dipole moments 2.15 D (for butadieneirontetracarbonyl) and 1.94 D (for the tricarbonyl analogue) did not permit *cis–trans* isomers to be distinguished[135].

More definite information was obtained for butadienylironoctacarbonyl, which on the basis of its low polarity ($\mu \simeq 0.9$ D) was assigned structure (XXXVII) with $Fe(CO)_4$ groups arranged on both sides of the plane of the butadiene ring[135].



(XXXVII) (XXXVIII) (XXXIX)

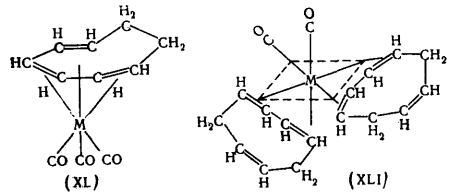
Complexes (XXXV)–(XXXVIII) are evidently the only exceptions among the carbonyl–alkenes where the diene occupies one coordination site: in all the other instances the diene acts as a bidentate ligand.

In the 3-vinylcyclohexeneirontricarbonyl complex the alkene is coordinated by both π-bonds with the formation of the complex (XXXVIII) with $\mu = 2.94$ D.[1]

On the basis of the dipole moment (4.9 D),[139] and the infrared[139] and NMR[140] spectra the (cyclo-octa-1,5-diene) metaltetracarbonyls are assigned the structure (XXXIX) with a boat conformation of the cycloalkene.

Clearly, an analogous structure can be assumed for cyclo-octa-1,5-dieneirontricarbonyl with dipole moment 3.1 D,[139] the infrared spectra[141] being consistent with this structure.

The comparatively high value of the dipole moment of cyclo-octatrienemolybdenumtricarbonyl $C_8H_{10}Mo(CO)_3$, 4.1 D, shows the coordination of the cycloalkene as 1,3,5-cyclo-octatriene (XL) and the displacement of the electron density from the cyclo-octatriene ring to the metal and further towards the carbonyl groups[142]. The lower moment for bis(cyclo-octatriene)molybdenumdicarbonyl $(C_8H_{10})_2Mo(CO)_2$, 1.96 D, can be explained by the participation of the 1,3,6-isomer in the complex formation[142]. Fischer and coworkers assume that the *trans*-arrangement of the 1,3-diene system is improbable. However, because of its comparatively low dipole moment (~ 2 D) the compound has been assigned the structure (XLI):[142]



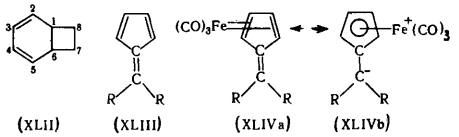
(XL) (XLI)

where M = Mo or W.

Two alkene carbonyl complexes of iron were also obtained by the reaction of a mixture of cyclo-octatriene isomers with $Fe(CO)_4$: a yellow liquid and red crystals[142]. By analogy with the molybdenum complexes the liquid product (dipole moment 2.37 D) was assigned the structure of a 1,3,6-cyclo-octatriene complex.

The solid, with a higher dipole moment (3.66 D) was assigned a structure with 1,3,5-configuration of the cyclo-octatriene ligand[142]. Later investigation of the chemical properties[143,144] and the infrared[144] and NMR[145] spectra showed that any isomerisation of cyclo-octatriene with iron carbonyls leads to bicyclo[4,2,0]octa-2,4-diene (XLII) of which the complexes under consideration are derivatives[143].

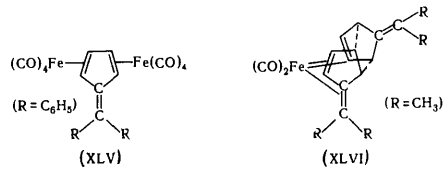
The π-system of the cyclopentadiene ring of the diphenylfulvenes was found to be convenient for the formation of alkene(carbonyl) complexes[146].



(XLII) (XLIII) (XLIVa) (XLIVb)

The values of the dipole moments of the diphenylfulveneirondi- and tricarbonyls reach 2.5–3.5 D[146] whereas diphenylfulvene itself (XLIII; R = C_6H_5) has a moment of 1.34 D[147] and its *p*-chlorophenyl derivative (XLIII, R = *p*-ClC_6H_4) 0.68 D.[18] These values of the dipole moments are connected with the contribution of the polar structures (XLIVb), which is especially significant for the *p*-chlorophenyl derivatives[146]. Weiss and Hübel[146] consider that the realisation of structure (XLIVb) is confirmed by the marked rise in dipole moment (XLIVa, R = *p*-ClC_6H_4) in comparison with the initial fulvene and complex (XLIVa, R = C_6H_5), whereas electron-withdrawing substituents in the phenyl nuclei of the ligand decrease the moment[146].

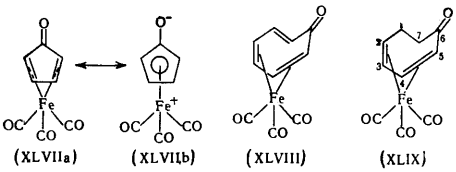
Diphenylfulvenedi-ironoctacarbonyl $C_{18}H_{14}Fe_2(CO)_8$ has moment 1.73 D, not greatly above that of free diphenylfulvene (1.34 D). Therefore the complex under consideration is assigned the structure (XLV) with symmetrically arranged $Fe(CO)_4$ groups, each of which is coordinated with one double bond of the diene ligand.



(XLV) (XLVI)

A quite unusual structure (XLVI) in which the exocyclic double bond of fulvene is utilised, is assigned to bis(dimethylfulvene)irondicarbonyl $[(CH_3)_2C{=}C_5H_4]_2Fe(CO)_2$ on the basis of the dipole moment (2.88 D)[148] and infrared spectra[146].

In the formation of mixed carbonyl complexes cyclopentadienone and tropolones can act as π-ligands[148–151]. The high values of the dipole moment of complex (XLVIIa), 4.4 D,[150] taken in conjunction with the infrared spectra[148,149] show the polarisation of the carbonyl group and the significant contribution of the polar structure (XLVIIb):

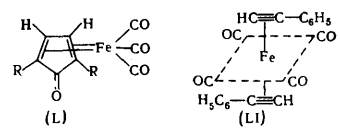


(XLVIIa) (XLVIIb) (XLVIII) (XLIX)

The ability of the iron cyclopentadienonecarbonyls to form adducts with acids and phenols of general formula $(CO)_3FeC_5H_4O.HX$, where X = Cl, Br, I, OAr and to give a negative reaction, characteristic of ketones, with phenyl- and 2,4-dinitrophenyl-hydrazines agrees with these suggestions[150].

However, this explanation can hardly be completely correct since the analogous complexes of tropoloneirontricarbonyl (XLVIII) with dipole moment 4.3 D show reactions typical of the keto-group[151]. The product of the non-polar hydrogenation of complex (XLVIII), cyclohepta-2,4-dienoneirontricarbonyl (XLIX) exhibits the same properties: at a high value of the dipole moment it forms the stable 2,4-dinitrophenylhydrazone[151] and has a C=O stretching frequency of 1661 cm^{-1}; the carbonyl group probably does not coordinate with the metal atom.

The reaction of pentacarbonyliron with phenylacetylene yields 2,5-diphenylcyclopentadienoneirontricarbonyl (L) with dipole moment 3.1 D.[152,153] This value eliminates the centrosymmetric structure (LI) suggested earlier[10,152]:



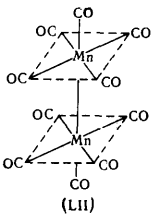
(L) (LI)

where R = C_6H_5.

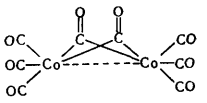
3. Polynuclear Carbonyls and Nitrosyls

The dipole moments of the dinuclear carbonyls of rhenium and manganese of composition $M_2(CO)_{10}$, determined in benzene, dioxan, and cyclohexane, have values close to 1.0 D,[103] although according to the infrared spectra[12,154–157]

and X-ray structural investigations[158,159] these complexes should have a symmetric structure[86].



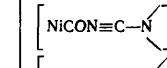
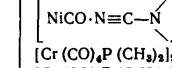
(LII)



(LIII)

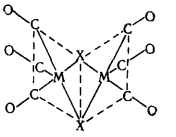
In this connection the assumption is made that the atomic polarisation should constitute 20–30% of the electronic: the dipole moment of both complexes should then become close to zero[103]. To explain the polarity (μ = 1.29 D)[160] of octacarbonyldicobalt $Co_2(CO)_8$ it was assumed that the CO bridges connecting the cobalt atoms are curved (LIII; C_{2v} symmetry)[14,154].

Table 2. Dipole moments of doubly charged complexes.

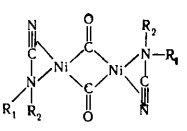
No.	Compound	Dipole moment in benzene, at 25°C, μ, D	Reference
1	$[Fe(CO)_3S]_2$	1.63	161
2	$[Fe(CO)_3Se]_2$	2.20	161
3	$[Fe(CO)_3SC_2H_5]_2$	2.69	161
4	$[Fe(CO)_3NH]_2$	3.28	162
5	$[Fe(CO)_3P(CH_3)_3]_2$	3.1	166
6	$[Fe(CO)_3P(C_2H_5)_3]_2$	3.6	166
7	$[Fe(CO)_3As(CH_3)_3]_2$	3.8	166
8	$[Fe(CO)_3Tep\text{-}C_6H_4OCH_3]_2$	3.00	124
9	$[Fe(CO)_4P(CH_3)_3]_2$	4.2	166
10	$[Fe(CO)_4Sn(C_4H_9)_2]_2$	0.8	116
11	$[Fe(NO)_2SC_2H_5]_2$	1.88	165
12	$[Fe(NO)_2SeC_2H_5]_2$	0.92	165
13	$[Fe(NO)_2P(C_6H_5)_3]_2$	2.53	164
14	$[Co(NO)_2Cl]_2$	1.04	165
15	$[Co(NO)_2Br]_2$	1.02	165
16	$[Co(NO)_2P(C_6H_5)_3]_2$	1.67	164
17	$[Mn(CO)_4P(OC_6H_5)_3]_2$	2.67	117
18	$[Mo(CO)_4P(CH_3)_3]_2$	1.9	167
19	$[Mo(CO)_4P(C_2H_5)_3]_2$	0.9	161
20	$[Mo(CO)_4As(CH_3)_2]_2$	0.9	161
21	$[Mo(CO)_5P(CH_3)_3]_2$	4.8	167
22	$[Mo(CO)_5P(C_2H_5)_3]_2$	3.9	161
23	$[NiCO\cdot N{\equiv}C{-}N(CH_3)_2]_2$	1.08	168
24		2.12	168
25		1.57	168
26	$[Cr(CO)_4P(CH_3)_3]_2$	1.0	167
27	$[Cr(CO)_4P(C_2H_5)_3]_2$	1.4	161
28	$[Cr(CO)_5P(CH_3)_3]_2$	4.6	167
29	$[W(CO)_4P(CH_3)_3]_2$	1.2	167
30	$[W(CO)_4P(C_2H_5)_3]_2$	0.6	161
31	$[W(CO)_4As(CH_3)_3]_2$	1.1	161
32	$[W(CO)_5P(CH_3)_3]_2$	3.9 4.6	161 167
33	$[W(CO)_5P(C_2H_5)_3]_2$	3.7	161
34	$[W(CO)_5As(CH_3)_2]_2$	3.9	161

Not only CO but also other groups (NH, SC_2H_5, SeC_2H_5, PMe_2,[161,162] PR_2,[163,164] and AsR_2 [163]), halogen atoms[165], and sulphur and selenium atoms[161], and also SnR_2 [116] can act as bridging ligands in polynuclear carbonyls. Table 2 gives the values of the dipole moments of complexes with these groupings.

Model (LIV), in which the two bridging groups and two iron atoms do not lie in the same plane, was proposed to explain the polarity of the externally non-symmetric carbonyls of the $[FeX(CO)_3]_2$ type[161]. This model has C_{2v} symmetry. A similar symmetry is evidently characteristic for $[Fe(NO)_2(SC_2H_5)]_2$,[165] the halogeno(nitrosyl) complexes of cobalt[165], and the tungsten and molybdenum carbonyls of general formula $[M(CO)_4ER_2]_2$.[117,161,167] X-ray diffraction showed a similar structure for $[Fe(CO)_3(SC_2H_5)]_2$.[169] In all the complexes considered the presence of bridging groups creates a certain rigidity of structure and increases their symmetry. In those dinuclear carbonyls where the dimerisation occurs through a metal–metal bond (Table 2, compounds 21–23, 32–34) there arises the possibility of free rotation around this bond, which leads to a decrease in the symmetry of the molecule and the appearance of a comparatively high dipole moment[161,167].



(LIV)

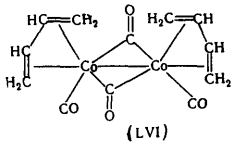


(LV)

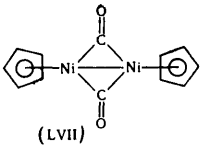
The presence of bridging CO groups was suggested on the basis of results obtained in the determination of dipole moments and investigations of the infrared spectra for the dialkylcyanoamido-complexes of nickel carbonyl (LV). The lone pair of electrons of the amine nitrogen and the π-electrons of the nitrile group take part in the formation of these complexes; the values of the dipole moments (1.5–2.0 D) are consistent with C_{2h} molecular symmetry[168].

The determination of dipole moments was an important tool for finding the structure of the polynuclear carbonyls containing organic π-ligands.

The high polarity (μ = 3.39 D) allows bis(butadiene-cobalt-tricarbonyl) to be assigned the structure with *cis*-arrangement of the CO ligands (LVI):[1,170] the dipole moment for the *trans*-configuration should be close to zero.



(LVI)

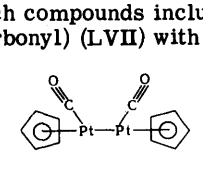


(LVII)

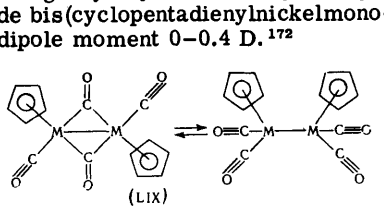
The considerable value of the dipole moment (3.02 D) of the compound bis(cyclo-octa-1,3,6-trienecobaltdicarbonyl) is connected with the angular structure of this complex[171].

The dipole moment method has proved extremely useful for solving problems of the presence or absence of carbonyl bridges in a series of dimers of cyclopentadienylmetalmonocarbonyls of general formula $[C_5H_5M(CO)]_2$. Two groups of complexes can be distinguished among these compounds: (1) those with a dipole moment close to zero, and (2) those which are polar, with a moment of ~ 2.0–3.0 D.

The first type of complex is credited with a rigidly symmetric structure, the dimerisation in which occurs by an M–M bond, and the "rigidity" by two carbonyl bridges. Such compounds include bis(cyclopentadienylnickelmonocarbonyl) (LVII) with dipole moment 0–0.4 D.[172]



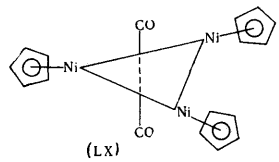
(LVIII)

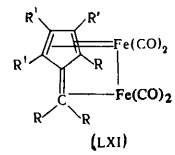


(LIX)

The appearance of polarity in the second group of complexes is connected with dimerisation solely by the M–M bond, around which free rotation is possible. The infrared and NMR spectra are inconsistent with carbonyl bridges and a symmetrical arrangement of the C=O groups in bis(cyclopentadienylplatinum-monocarbonyl)(LVIII) with dipole moment 2.6 D.[173]

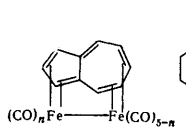
Other relationships are observed between the values of the dipole moments and structure of the dimers of cyclopentadienylmetaldicarbonyls $[C_5H_5M(CO)_2]_2$. In this instance the complexes with the pure M–M bond (M = Os)[174] and the compounds with an M–M bond fixed by carbonyl bridges (M = Fe)[175] have appreciable dipole moments, respectively 2.6 and 3.1 D, due to the breaking of the carbonyl bridges in the solution and the formation of polar *cis*-structures (LIX), observed in detailed infrared spectroscopic investigations[176].

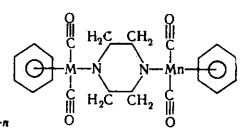

(LX)


(LXI)

The zero value of the dipole moment of the polynuclear nickel complex, $(C_5H_5)_3(Ni_3(CO)_2$, indicated the centrosymmetric structure (LX),[172] and this was also confirmed by X-ray diffraction[15].

The complexes of $Fe_2(CO)_9$ with substituted fulvenes obtained by Weiss and Hübel are interesting, the fulvenes evidently acting as bidentate ligands. The polarity (3.5–4 D)[146] and the absence from the infrared spectra of bands for carbonyl bridges suggests that the probable structure for this group of complexes is (LXI). However, the number of CO groups at the iron atoms (3 : 3 or 4 : 2, as in (LXI) —remains uncertain[146].


(LXII)


(LXIII)

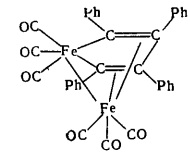
Azulene can also take part in the formation of similar complexes[177]. On the basis of the considerable polarity (μ = 3.97 D) and absence of absorption in the region for bridging CO groups, Wilkinson and coworkers ascribed the structure (LXII) to the complex with general formula $C_{10}H_8Fe_2(CO)_5$.[177]

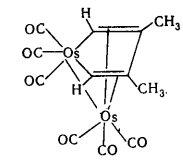
The low dipole moment (~ 1 D) of the complex (LXIII) agrees well with its symmetric structure[178].

The reaction of acetylene[10,175,179] and its derivatives with iron carbonyl is very interesting. Two centrosymmetric structures were proposed for the products of the reaction of iron tetracarbonyl with acetylene and diphenylacetylene, of general formula[180]:

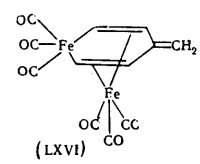
$$Fe_2(CO)_6(RC{\equiv}CR)_2.$$

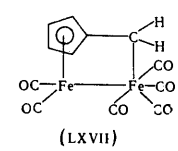
However, the high values of the dipole moments of these complexes (μ = 2.86 D for R = H;[175] μ = 3.3 D for R = C_6H_6[180]) are against their symmetric structure. It transpired that it is more correct to regard these compounds as derivatives of tricarbonyl(ironcyclopentadienyl)irontricarbonyl (LXIV),[180] particularly as structures similar to (LXIV) have been demonstrated by X-ray diffraction for a series of reaction products of acetylenes with iron[181–183] and osmium[182] (LXV) carbonyls.


(LXIV)


(LXV)

A non-zero value of the dipole moment allows conclusions to be drawn about the absence of a centre of symmetry for compounds[175] of the general formula $(C_2H_2)_3Fe_2(CO)_6$. One of these with dipole moment 1.7 D was given the structure (LXVI) because of its paramagnetism[175]; its isomer with a higher dipole moment (3.41 D) was assigned the structure (LXVII).[175]

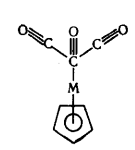

(LXVI)

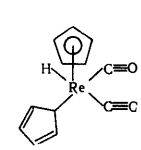

(LXVII)

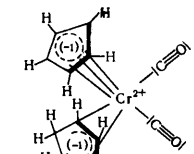
4. Cyclopentadienyl and Arenecarbonyl Compounds

The values of the dipole moments of the monocyclopentadienylmetal carbonyls lie within the range 2.9–3.5 D and to a first approximation vary little with the number of carbonyl groups in the complex[96,184,185]. The value of the moment also varies little on replacing the carbonyl groups by nitrosyl: cyclopentadienylchromiumdicarbonylmononitrosyl π-$C_5H_5Cr(CO)_2(NO)$ has μ = 3.2 D.[96]

These values of the dipole moment allow the M–C_5H_5 bond moment of the bond to be estimated as ~ 2.0–2.5 D,[96] if it is assumed that the moment of the M–C–O fragment does not exceed 0.5–0.8 D.[96,105] The high polarity of the π-complexes of this type is connected with the asymmetry of their structure, for example (LXVIII).[1,6,86]


(LXVIII)


(LXIX)


(LXX)

The dipole moments of the π-cyclopentadienylmetalcarbonyls are almost independent of the solvent, which is explained by the coordination saturation of the metal atom in these compounds[185]. Bis(cyclopentadienyl)rheniumdicarbonyl hydride $(C_5H_5)_2ReH(CO)_2$, which belongs to this type of complexes, was assigned structure (LXIX) with π- and σ-bonded cyclopentadienyl rings on the basis of its high polarity (μ = 3.85 D)[31,186,187] and NMR and infrared spectra[188]. Structure (LXX), in which the CO groups are

Table 3. Dipole moments of arenemetaltricarbonyls.

No.	Formula	Arene	Solvent	P_A, % of P_E	μ, D	Reference
1	$C_6H_6Cr(CO)_3$	benzene	B	15	5.08	193
			B	15	4.92	31
				15	4.81	191
			C	15	4.31	31
			H	15	4.38	191
			D	15	5.33	191
2	$C_7H_8Cr(CO)_3$	toluene	B	—	5.26	193
			B	15	5.20	31
			B	—	5.12	191
			H		4.38	191
			D		5.40	191
3	$C_8H_{10}Cr(CO)_3$	*p*-xylene	B	—	5.52	193
			B	15	5.39	31
			H	—	4.95	191
			B	—	5.41	191
			D	—	5.55	191
4	$C_8H_{10}Cr(CO)_3$	*o*-xylene	B	15	5.41	31
5	$C_8H_{10}Cr(CO)_3$	*m*-xylene	B	15	5.37	31
6	$C_9H_{12}Cr(CO)_3$	mesitylene	B	—	5.52	193
			B	15	5.56	31
			B	—	5.59	191
			H	—	5.22	191
			D	—	5.72	191
7	$C_{10}H_{14}Cr(CO)_3$	1,2,4,5-tetramethylbenzene	B	—	6.04	193
8	$C_{12}H_{18}Cr(CO)_3$	hexamethylbenzene	B	—	6.48	193
			B	15	6.22	31
			B	—	6.27	191
			H	—	5.94	191
			D	—	6.35	191
9	$C_{10}H_8Cr(CO)_3$	naphthalene	B	15	6.33	31
			B	—	5.02	191
			B	—	5.13	194
			H	—	4.86	191
			D	—	5.00	191
10	$C_{12}H_{10}Cr(CO)_3$	biphenyl	B	—	5.33	193
11	$C_{14}H_{10}Cr(CO)_3$	anthracene	B	—	5.20	195
12	$C_{14}H_{10}Cr(CO)_3$	phenanthrene	B	—	5.03	195
13	$HOC_6H_5Cr(CO)_3$	phenol	B	15	5.13	31
14	$CH_3OC_6H_5Cr(CO)_3$	anisole	B	—	5.43	193
			B	15	5.26	31
15	$H_2NC_6H_5Cr(CO)_3$	aniline	B	15	5.40	31
16	$(CH_3)_2NC_6H_5Cr(CO_3)$	dimethylaniline	B	—	6.30	193
17	$ClC_6H_5Cr(CO)_3$	chlorobenzene	B	—	5.08	193
			B	—	4.21	192
			B	—	4.53	196
18	$IC_6H_5Cr(CO)_3$	iodobenzene	B	—	4.59	196
19	$BrC_6H_5Cr(CO)_3$	bromobenzene	B	—	4.65	196
20	$pCl_2C_6H_4Cr(CO)_3$	*p*-dichlorobenzene	H	—	3.72	191
			B	—	4.00	
			D	—	4.20	
21	$FC_6H_5Cr(CO)_3$	fluorobenzene	B	—	4.91	193
			B	15	4.75	31
			B	—	4.51	196
22	$F_2C_6H_5Cr(CO)_3$	*p*-difluorobenzene	H	—	3.97	191
			B	—	4.40	
			D	—	4.67	
23	$CH_3O_2C—C_6H_5Cr(CO)_3$	methyl benzoate	B	15	4.47	31
24	$p(CH_3O_2C)_2C_6H_4Cr(CO)_3$	dimethyl terephthalate	B	—	3.52	192
25	$p(CH_3)_2C_6H_4Mo(CO)_3$	*p*-xylene	H	—	5.75	191
			B	—	6.06	
			D	—	6.25	
26	$p(CH_3)_2C_6H_4W(CO)_3$	*p*-xylene	H	—	5.86	191
			B	—	6.23	
			D	—	6.53	
27	$SeC_4H_4Cr(CO_3)$	selenophen	B	—	5.55	196
28	$2.5\text{-}(CH_3)_2SeC_4H_2Cr(CO)_3$	2,5-dimethylselenophen	B	—	6.00	196
29	$SC_4H_4Cr(CO)_3$	thiophen	B	—	5.54	196

arranged in the *cis*-position in relation to one another and the coordination number of the chromium is seven, is proposed[189] for cyclopentadienyl(cyclopentenyl)chromium-dicarbonyl $(C_5H_5)(C_5H_7)Cr(CO)_2$, from consideration of the vibrational and NMR spectra and the value of the dipole moment (3.5 D).

Arenechromiumtricarbonyls§ of the general formula $XArCr(CO)_3$, in distinction from the bisarene complexes of chromium, exhibit considerable polarity (the values of their dipole moments vary within the range 4.5–6.5 D, see Table 3). This value cannot be connected with a small moment of the C–O group (0.8 D) and it is explained by the polarisation of the metal–arene bond[31,71,191,192].

It was logical to assume that the presence of this polarisation should lead to an increase in the dipole moment of the arenechromiumtricarbonyls containing electron-donating substituents in the benzene rings and a decrease in polarity when the substituents are electron-withdrawing[31,191,193]. The values of the dipole moments of the complexes with electron-donating (compounds 2–16, Table 3) and electron-withdrawing (compounds 17–22) substituents confirm the hypothesis and there is a satisfactory correlation between Hammett's σ constants, the dipole moments, and the displacements of the C–O stretching frequencies[192].

Randel and Sutton[193] determined the dipole moments of a group of arenechromiumtricarbonyls containing from one to six methyl groups in the benzene nucleus and concluded that the moments found experimentally (in benzene) agree satisfactorily with the values calculated by the formula $\mu = \mu_0 + 0.23n$ (where μ_0 is the moment of benzenechromiumtricarbonyl and n the number of methyl groups). It was shown later that for other solvents also similar relations can be found: $\mu = \mu_0 + 0.26n$ (heptane) and $\mu = \mu_0 + 0.20n$ (dioxan)[191]. However, if it is remembered that the dipole moment values of the methyl-substituted arenechromiumtricarbonyls obtained for one or another solvent by different authors vary by 0.2–0.3 D (Table 3), the above relations must be considered to be extremely approximate. With the arenechromiumtricarbonyls the solvents have a considerable effect on the value of the dipole moment: the greatest moment is observed in solvents such as dioxan and the least in heptane; benzene occupies an intermediate position[191]. This peculiarity in the behaviour of the arenechromiumtricarbonyls, the aromatic rings of which can behave as potential acceptors of electrons is thought by Strohmeier to be explained by the formation of donor–acceptor compounds between the complex and the solvent[191]. Such an explanation agrees well with the fact that the difference in the values of the dipole moments ($\Delta\mu$) determined in dioxan and in heptane gradually decreases with increase in the number of electron-donating groups in the aryl nuclei of the complexes and reaches a minimal value for hexamethylbenzenechromiumtricarbonyl[191]. Furthermore, from this position it is not clear why $\Delta\mu$ decreases, not increases, for arenechromiumtricarbonyls with electron-acceptor substituents in the aryl nuclei (chlorine, fluorine[191], and especially an ester group[194]), and why the value of $\Delta\mu$ for naphthalenechromiumtricarbonyl is extremely low (0.14 D).[191,195]

A comparison of the dipole moments of the *p*-xylenetricarbonyl complexes of chromium, molybdenum, and tungsten (Table 3) shows that in the series Cr → Mo → W the values of the moments increase with increasing acceptor strength in the order $Cr(CO)_3$, $Mo(CO)_3$, $W(CO)_3$.[191]

The dipole moments of the cyclopentadienyl and arenemetal carbonyls of the general formula $RM(CO)_2L$, where M = Cr and L is a nitrogen base, $P(C_6H_5)_3$, are $SO_2(CH_3)_2$ groups[115], and also π-ligands (alkenes, alkynes)[197] have been determined. The results have been used to calculate

§ A review on substituted carbonyls of the metals of Group VIb appeared recently[190].

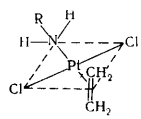
the partial dipole moments μ(M–L) of the metal–donor bond and to establish a correlation between these quantities and the stretching frequencies of the carbonyl groups of the complexes[197].

IV. COMPLEXES OF METAL SALTS WITH UNSATURATED HYDROCARBONS

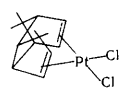
1. Complexes of Alkenes

The dipole moments of the purely alkenic complexes bis(ethyleneplatinum chloride) $(C_2H_4PtCl_2)_2$ [198] and bis-(ethylene) platinum(II) dichloride[199] have not been measured.

In 1947 Syrkin and Shidlovskaya[200] determined the dipole moment of the simplest representative of the alkene complexes (LXXI; R = H) of platinum(II) chloride $C_2H_4PtCl_2NH_3$, which was investigated in detail later by Chatt and coworkers[198,199].



(LXXI)



(LXXII)

The values obtained for complexes of the type (LXXI) (for R = p-$CH_3C_6H_4$ the dipole moment is 2.35 D; for R = p-ClC_6H_4, 1.79 D) correspond to the difference in moments $\mu_{(N-Pt)} - \mu_{(C_2H_4-Pt)}$ and since $\mu_{(N-Pt)}$ has been evaluated[201] as ~ 6 D the moment $\mu_{(C_2H_4-Pt)}$ should be 4 D.[186] Evidently this value characterises a donor–acceptor bond produced by the bonding of the π-orbital of ethylene and the dsp^2-orbitals of platinum. A bond of this type is extremely polar, therefore the comparatively low value of the dipole moment is explained by the formation of an additional dative bond from the Pt atom to the antibonding π^*-orbital of the alkene ligand[198].

This treatment of the nature of the metal–alkene bond¶, which is confirmed by X-ray diffraction[204,205] and electron diffraction investigations[206], by the prominant trans effect of the alkenes[203,207] and also by calculated data[208], is now widespread.

Determination of the dipole moment of the complex of platinum(II) chloride with bicyclopentadiene led to a conclusion about the coordination at the π-bond of the alkene[209]. For 50 years this compound had been ascribed a structure with a C–M σ-bond[210] and it was only in 1956 on the basis of the considerable dipole moment (μ = 13 D) and the infrared spectra that it was given structure (LXXII).[209]

The complexes of $PtCl_2$ with hexa-1,5-diene (6.1 D) and cyclo-octatetraene (7.0 D)[211] should probably also have structures similar to (LXXII). In the latter instance the appreciable value of the dipole moment is thought by Jensen[211] to be connected with the fact that the cyclo-octatetraene in the complex has the "boat" conformation and this is also detected in the spectroscopic investigations[212]. According to the results of crystal-chemical investigations[213] dipenteneplatinum dichloride $C_{10}H_{16}PtCl_2$, norbornadiene palladium dichloride[214] $C_7H_8PdCl_2$, and dimeric cyclo-octa-1,5-dienerhodium chloride[215] have structures similar to (LXXII).

In connection with the increasing interest in the mechanism of cationic polymerisation[216,217] papers devoted to a study of the polar properties of complexes of tin(IV) chloride with unsaturated compounds[218,219] have recently appeared.

¶ The earlier work of Gel'man[202,203] is interesting in this connection.

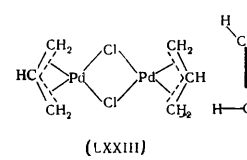
Using a method of dielectrometric titration Gol'dshtein and coworkers determined the values of the dipole moments of complexes of tin(IV) chloride with styrene (0.73 D), stilbene (0.75 D), and 1,1'-diphenylethylene (1.09 D).[218,219] The dipole moments of such complexes of $SnCl_4$ with alkenes are distinguished from the moments of the free ligands by 0.4–0.7 D and it was concluded that the products of the reaction of tin(IV) chloride with unsaturated hydrocarbons are π-complexes[218].

The existence of such complexes was shown not only in the determination of the dipole moment but also by a spectroscopic method[220,221]. Furthermore it must be borne in mind that the interpretation of the values of the dipole moments of these complexes in benzene is difficult, since according to some data $SnCl_4$ itself has a moment of 0.8–0.95 D in this solvent[16,17].

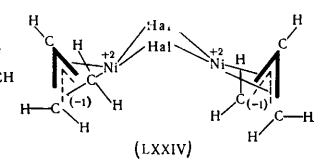
2. π-Allyl Complexes

The structure of the π-allyl complexes of the transition metals has now been adequately studied[222,223]. The largest number of dipole moment data are for bis(allylpalladium chloride) $(C_3H_5PdCl)_2$,[224,225] its methylallyl $(C_4H_7PdCl)_2$ [226] and phenyl $(C_9H_9PdCl)_2$ [227] analogues, and bis-(π-allylnickel halides) $(C_3H_5NiX)_2$.[228,229] The participation of the π-electrons of the allyl radical in the formation of such complexes is now no longer open to doubt[230–233]: it has been demonstrated in the study of the infrared[234] and NMR [235] spectra of the allyl complexes of palladium chloride, by X-ray structural investigations[236–238], and in other ways.

The dimeric nature of these complexes[225] and the results of X-ray structural analyses[236–238] allow structure (LXXIII) with μ-halogeno bridges to be ascribed to complexes of this type.



(LXXIII)



(LXXIV)

For the strictly planar structure of type (LXXIII) the dipole moment should be close to zero. Starting from this assumption, Syrkin and coworkers assumed that the nonzero value of the dipole moment of bis-(π-allylpalladium chloride) 2.23 D (for the α form) and 3.4 D (for the β) belong to the monomer[225]. However, other authors[226] state that the moment of 2.2 D obtained for bis-(π-methylallylpalladium chloride) relates to a dimer. A similar opinion is also expressed for the allyl complexes of the nickel halides[229]: the dipole moment of 1.62 D for bis-(π-allylnickel iodide) and 1.31 D for bis-(π-allylnickel bromide) are connected with dimeric molecules which exist in benzene and cyclohexane solutions.

The question naturally arises as to the reason for the polarity of the externally symmetrical dimeric π-allyl complexes of the metal halides.

The hypothesis of the donor–acceptor interaction of the molecule of the complexes (LXXVII) with the π-system of the solvent, which could have a considerable effect on the value of the moment, is improbable here, since in cyclohexane the dipole moment of this type of compound is considerable (for example, for bis-(π-allylnickel iodide) it is 1.48 D.[229] Fischer considers that to explain these values of the dipole moments of the dimeric π-allylnickel halide molecules they must have the structure (LXXIV) in

which the halogen bridges cause curvature of the molecule, destroying its symmetry[229].

Similar ideas could evidently be extended to the butadiene complexes of palladium and platinum chlorides, the structure of which has been little studied.

The dipole moments (~ 3.5 D) of the π-allyl complexes of rhodium and palladium of the type

$$[E(C_6H_5)_3]Cl_2M\text{-}\pi\text{-}C_4H_7,$$

where E = P, As, Sb, have also been determined (~ 3.5 D).[239]

In conclusion it must be noted that the structural assignment of the products of the reaction of metal chlorides with allyl hydrocarbons is of considerable importance for finding the mechanism of oxidation of alkenes[240] and for various polymerisation processes[231].

V. COMPLEXES OF THE HALIDES OF THE ELEMENTS OF GROUPS III–V WITH AROMATIC HYDROCARBONS

Interest in the complexes of metal halides with aromatic hydrocarbons has arisen in connection with the study of the mechanisms of a large number of catalytic reactions which take place with participation of aluminium chloride[241,242] and the halides of other metals[243].

A principal part in solving the problem of the existence of metal halide complexes with aromatic hydrocarbons and of their nature was played by dipole moment studies on halides in various solvents. Even in the first papers of Ulich and Nespital it was shown that aluminium bromide, which is almost non-polar in carbon disulphide, has a high dipole moment (4.9–5.2 D) in benzene[244,245]. It was found later that in aromatic solvents (benzene, toluene, *p*-xylene) the dipole moments of aluminium bromide reach values of ~ 5–6 D[248] whereas in cyclohexane[249], carbon disulphide, bromine[248], and also the melt[246], the values of μ are close to zero. These results agree with ideas about the dimerisation of $AlBr_3$ in these solvents. X-Ray structural[250], electron diffraction[251,252], and spectroscopic[253] investigations lead to the same conclusion.

The high values of the dipole moments of aluminium bromide in benzene[244–248,246] naturally raised the question of the reasons for its polarity in non-polar solvents.

The first attempt to explain this was made by Ulich and Nespital, who considered that in the benzene solution dissociation of the dimeric molecules of aluminium halides took place, leading to the appearance of non-symmetric monomers of $AlBr_3$ with a structure distorted under the influence of the solvent[244,245]. The appreciable dipole moment of aluminium iodide[246] and gallium chloride[254] in benzene (2.5 and 3.05 D respectively) responded to analogous treatment. In later investigations[246–248] although the dissociation of the dimeric molecules of aluminium halides in benzene was not contradicted, the high values of the dipole moments were connected with the formation of complexes of the monomeric molecules of the halides with the solvent.

Evidence in support of the existence of such complexes is provided by the results of the physicochemical analysis of the $AlBr_3$–C_6H_6 system[225] and the results of spectroscopic[256], thermochemical, and electrochemical[247] investigations.

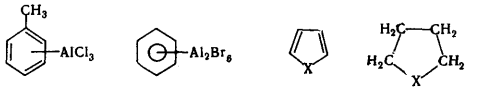
The high values of the dipole moments of antimony trichloride (~ 4.0 D)[257–259] and tribromide (3.28 D)[259] in benzene also show the interaction of SbX_3 with the solvent, leading to the formation of a complex, which is also observed by thermal analysis[260] and spectroscopy[261,262].

Similarly it is possible to explain the polarity of thallium(III) chloride (3.93 D)[263] and silver perchlorate (4.7 D)[264] in benzene, which in the last instance agrees with the existence of a molecular compound $AgClO_4.C_6H_6$[265] and also the appearance of non-zero moments for the symmetric molecules of tin(IV) chloride in benzene[266,267] and for the $SnCl_4$–naphthalene complex[268].

All the above results leave no doubt about the ability of aromatic hydrocarbons to form complexes with metal halides.

Many investigations[241,269–271] were made to explain the nature of these complexes and it became understandable only comparatively recently[271].

It is now generally accepted that aromatic compounds form π-complexes with metal halides owing to the interaction of the π-electrons of the aromatic system and the vacant orbitals of the metals. For example, the complex of toluene with aluminium chloride is ascribed the structure (XXV)[270]:



(LXXV) (LXXVI) (LXXVII) (LXXVIII)

where X = O, S.

Some recent investigations of the problem by Romm and Gur'yanova are of special interest[272]. They showed that in thoroughly dried benzene aluminium bromide keeps a dimeric structure and its dipole moment does not exceed 1 D. The authors consider that the π-complex of benzene with aluminium bromide has structure (LXXVI), and the high values of the dipole moments obtained earlier for $AlBr_3$ in aromatic solvents are connected with the formation of a ternary complex $Al_2Br_6.HBr.nAr$.[272] The results of this investigation, although not denying the possibility of the formation of π-complexes of the metal halides with aromatic hydrocarbons, merit critical examination of the values obtained earlier for the dipole moments of halides in aromatic solvents[16–17].

In determining the dipole moments of complexes of tin(IV) chloride with furan and thiophen (LXXVII) it was found that both the value of the moment of the complex and its increase during complex formation are considerably less than for saturated heterocycles (LXXVIII).[218,273] These results led to the conclusion that thiophen and furan form π-complexes with $SnCl_4$ (the dipole moment of the thiophen complex is 1.73 D, that of furan 0.99 D), but thiophan (5.0 D) and tetrahydrofuran (5.94 D) give complexes with a donor–acceptor bond owing to the *p*-electrons of the sulphur or oxygen atoms[273]. The infrared spectra of the complexes of $SnCl_4$ with thiophen and thiophan support these ideas[274].

It is remarkable that according to dielectric constant measurements of titanium(IV) chloride does not form π-complexes with benzene[275] and thiophen[276]. However, thermal analyses[277,278] and spectroscopic[278] and magnetic (EPR)[279] investigations show that $TiCl_4$ forms π-complexes with aromatic systems including benzene[279]. Therefore it must be borne in mind that in instances when the increase in dipole moment on going from the ligand to the complex is exceptionally small (< 0.5 D), the value of the moment cannot serve as a definite criterion for the absence of complex formation in the system. Only a combination of various physicochemical methods permits the behaviour of the compounds in solution to be judged.

In conclusion we note that not only metal halides but also a series of organometallic compounds are capable of

forming π-complexes with aromatic hydrocarbons. The same conclusion was reached from the results of Stromeier's work, which shows that the dipole moment of organometallic compounds in benzene is always greater than the value obtained in measurements in hexane, heptane, carbon disulphide, and other indifferent solvents [31,191,280,281].

VI. POLYMETALLIC $\pi\sigma$-COMPLEXES

Because of the rapid development of physicochemical and structural investigations in the field of bimetallic and polymetallic $\pi\sigma$-complexes [282,283], the polar properties of the organometallic compounds containing transition (M) and non-transition (M') metals are now being studied.

Kahn and Bigorgne [284,285] determined the dipole moments of bimetallic carbonyls of the type $(CO)_4Co.MX_3$, $(CO)_4Fe(MX_3)_2$, $[(CO)_4FeM'X_2]_2$, where M = Si, Ge, Sn, Pb; X = Cl, Alk, Ar, OMe.

From these results, detailed infrared investigations, and the assumption that the transition metal atom in these complexes is electrically neutral, the authors also determined the structure, found more accurately the nature of the M–M' bond [sic], and compared it with the bond in the $(CO)_4Fe–PX_3$ complexes.

On the basis of the dipole moments [286] of the recently prepared [287] carbonyl-π-cyclopentadienyls of the general formula $[\pi\text{-}C_5H_5Fe(CO)_2]_nSnX_{4-n}$, where X = Hal, Alk, Ar, conclusions were drawn about the monotonic increase in the moment with increase in the volume of X and the effect of the substituent on the polarity of the fragment $[\pi\text{-}C_5H_5Fe(CO)_2]$–Sn was discussed. This increase in the dipole moment is evidently connected with the approximation of the Fe–Sn–Fe angle to the regular tetrahedral angle (according to X-ray structural investigations [288–291] this angle is 124–126°).

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New information has recently appeared on the study of the structure of π-complexes by the dipole moment method. The value $\mu = 1$ D allows the *cis* structure to be ascribed to pentacarbonylbis(cyclopentadienyl)vanadium $(C_5H_5)_2V_2(CO)_5$; [292] the *trans*-configuration should be without a dipole moment. A centrosymmetric structure agrees with the insignificant value of the moment of the dimer of bis(cyclopentadienyl)platinum, $[Pt(C_5H_5)_2]_2$. [293]

The dipole moment method showed that the monocarbonyls [294] and mononitrosyls [295] of rhodium(I) and rhodium(III) of the general formulae $MX(CO)L_2$ and $MX_3(EO)L_2$ (where X = Cl, Br, I, SCN; L = PR_3, AsR_3) have the *trans*-structure. Analogous complexes of ruthenium have been isolated as *cis*- and *trans*-isomers [296].

A *trans*-arrangement of the PR_3 groups and *cis*-halogens is characteristic for dicarbonylphosphinic complexes $MX_2(CO)_2(PR_3)_2$ (M = Fe, Ru, Os), [297] but only the *cis*-structure for $[PtX_2CO(PR_3)]$. [298]

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Progress in the Synthesis of Perfumes Based on Pinenes†

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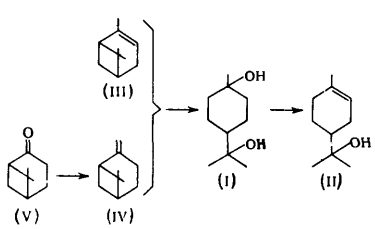
Turpentine was known in far antiquity. As is well known, it was obtained by steam distillation of various types of pine. Rosin and resins are obtained simultaneously.
All these products were used in the construction of ships. Turpentine was first produced in the XVIth century in North America, where there were vast areas of pine forests in North and South Carolina, Georgia, Alabama, and Virginia and where there was a market for these products, and they became widespread in the XVIIth century. The use of turpentine for the production of varnishes, paints, etc. began about 1830-1840.
There is a bibliography of 119 references.

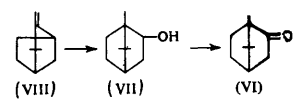
1. Turpentine and the Chemistry of Perfumes

Turpentine was first used as a raw material for the manufacture of perfumes at the end of the XIXth century. In 1827 Vogel obtained terpene (I), which Tilden in 1878 and Wallach in 1885 dehydrated to terpineol(II), and Flavitskii obtained terpineol directly from turpentine in 1879. In France the industrial production of terpineol was the consequence of work carried out by Bouchard and Bouari (1866) and Lafonte (1889).

The structure of α-pinene (III), the principal constituent of turpentine, was suggested by Wagner in 1894 and firmly established by Bayer two years later. The structure of β-pinene (IV) was established by Wallach in 1907 as a result of the synthesis of this terpene from norpinone (V). The first accurate analysis of a mixture of α- and β-pinenes was effected by Darmu in 1911 on the basis of measurements of optical rotatory dispersion.



Camphor (VI) was known in the Far East before recorded time. It was introduced into Europe by the Arabs. Reluz obtained it by the oxidation of borneol (VII) in 1841. At the end of the last century camphor became an important raw material for the manufacture of celluloid and smokeless powders. Bredt established the structure of camphor in 1893, but its synthesis, effected from the pinenes through the intermediate production of camphene (VIII), borneol, and isoborneol, was used industrially only until 1920.



Up to 1940 the pinenes were used for the production of terpineols, borneol, isoborneol, and their esters, and camphor. The position then changed sharply. This progress was due to the efforts of the producers of turpentine to increase its consumption and thanks to the wish of the synthetic perfumes industry to be freed from the use of natural ester oils, the difficulty of supply, variable quality, and high cost of which hindered the further development of this sector of industry.

I will not dwell on the papers dealing with the development of the chemistry of camphene, borneol, isoborneol, and camphor, and also terpenophenols, since most of the terpenophenols were first obtained in the USSR at the All-Union Scientific Research Institute for Synthetic and Natural Perfumes, where in this field also very interesting work is now being carried out.

This review will give the progress reached in effecting the opening of the bicyclic system of the pinenes and their derivatives into compounds of the monocyclic and aliphatic series.

The acid-catalysed decyclisation was effected even longer ago, since the production of terpineols was realised

† Paper read at the All-Union Scientific Research Institute of Synthetic and Natural Perfumes, Moscow, 1967.

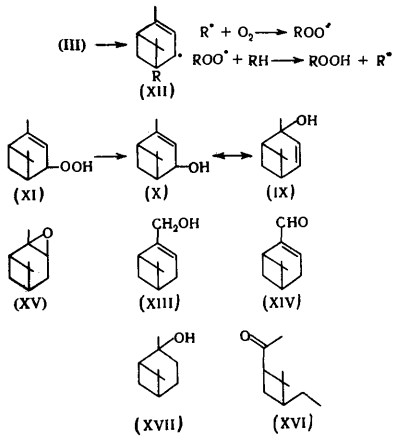
by industry seventy-five years ago. The application of this reaction to bicyclic derivatives of pinenes led to new methods for the production of menthones, menthols, carbeols, and carbone. However, the most progress was achieved in decyclisation by the pyrolysis of pinenes, pinanes, verbenols, and pinanols. These reactions opened the way to the production of aliphatic terpenes and their derivatives, such as linalool, geraniol, nerol, α- and β-citronellols, α- and β-elgenols, α- and β-citrals, citronellals, α- and β-elgenones, hydrohydroxycitronellal, and pseudoionones. The syntheses of these substances also open new paths for the production of menthols.

Many of these syntheses could not be carried out without the development of new methods for the production of verbenols, pinanols, and other similar compounds based on the production of oxides and hydroperoxides.

2. Production of Oxides and Hydroperoxides

The oxidation of α-pinene with or without the use of photosensitizers followed by the reduction of the hydroperoxides formed gives pin-3-en-2-ols (IX) and their allyl isomers—verbenols (X)—pinan-2-ols (XVII), and also verbanols.

According to Dupont[1], the primary products of the oxidation of α-pinene (III) are verbenyl hydroperoxides (XI), which are catalysts for the formation of the free radicals (XII), which initiate chain reactions. The mechanism of these reactions was also studied by Schenk and coworkers[2].



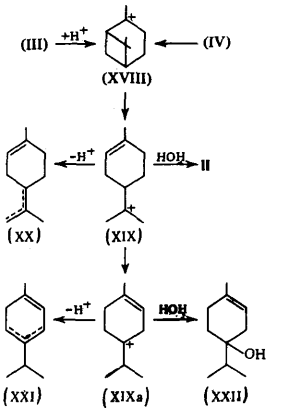
The production of hydroperoxides is accompanied by the formation of pinene oxides by the Prilezhaev reaction. As a result of all the reactions in the oxidation of α-pinene (III) after the reduction of the hydroperoxides a mixture is obtained which contains pin-3-en-2-ol (IX) (predominantly the *cis*-isomer), verbenols (X), verbenone, myrtenol (XIII), myrtenal (XIV), and α-pinene oxide (XV).[3,4] Here (−)α-pinene corresponds to (+)-pinenols, (−)-*trans*-verbenol, (+)-*cis*-verbenol, (−)-verbenone, and (+)-α-pinene oxide. The pinenols can be isomerised into the verbenols (X) by the action of hot water or dilute alcohols. The hydrohalogenation of verbenol leads to verbenyl halides, acetylation with acetic anhydride in the presence of sodium acetate gives *trans*-verbenyl acetate principally. Oxidation with chromium(VI) oxide leads to verbenone[5,6]. The hydrogenation of verbenols over copper chromite at 200°C leads to the formation of a mixture of isoverbanol and neo-isoverbanol[7].

Fischer and coworkers[8] studied the formation of hydroperoxides of pinanes. A product containing 85–90% hydroperoxide is obtained at 40–45% oxidation in 85–86% yield on the pinane used. The decomposition of the hydroperoxides in the presence of sodium methoxide leads to both 1-aceto-3-ethyl-2,2-dimethylcyclobutane (XVI) and pinan-2-ol (XVII) in 50% yield.

3. Decyclisation Catalysed by Acids

Although the opening of the four-membered ring of pinenes by acids has long been known[9,10] its mechanism was established with certainty only in 1947, by Moser[11,12]. In the presence of a proton α-pinene (III) or β-pinene (IV) form a carbonium ion (XVIII). The breaking of the four-membered ring is accompanied by transfer of the positive to the $C_{(8)}$ of the *p*-menthane system and the formation of a double bond in position 1 (XIX). This carbonium ion can be isomerised into (XXa). The removal of a proton leads either to the formation of dipentene and terpinolene (XX) or α- and β-terpineols (XXI). The migration of a double bond to $C_{(2)}$ leads to isoterpinolene and *p*-mentha-2,4-diene.

In the presence of OH ions α-terpineol (II) and terpin-1-en-4-ol (XXII) are formed:



The formation of the terpene (I) proceeds with the intermediate production of a double charged ion (XXIII). Its reaction with water and subsequent dehydration leads to α-, β-, and γ-terpineols, (II), (XXIV), and (XXV).

The formation of terpenes, which is accompanied by the formation of terpene (I) or terpineols, was long considered undesirable. It is now used for obtaining methols through menth-3-ene.

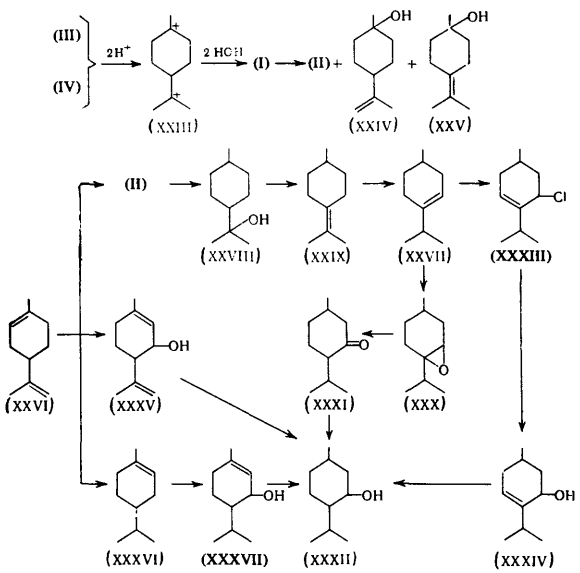
A good yield of monocyclic terpenes with a trace of camphene as impurity is obtained in the treatment of pinenes with ion-exchange resin or aluminosilicate (zeolite)[11a]. By carrying out the reaction at a certain temperature, up to 75% limonene or dipentene (XXVI) can be obtained. Limonene (XXVI) exhibits an angle of rotation opposite to that of α-pinene (III), and the same as β-pinene (IV). The optical purity is retained well.

A mixture of monocyclic terpenes with *p*-cymene and camphene as impurities undergoes disproportionation and hydrogenation. Bain and Gary[13] achieved the partial disproportionation in the presence of nickel formate, obtaining menth-3-ene in good yield. Camphene and α-pinene remained unchanged.

Partial hydrogenation over nickel at a low temperature leads to the formation of a mixture[14] of menth-2-ene and menth-4-ene. The latter readily isomerises into menth-3-ene (XXVII) on heating or under the action of acids[15]. As a result, a mixture of menthenes and *p*-cymene is obtained[16-18].

This method of synthesis of menth-3-ene is considerably more economical than the synthesis based on the dehydration of dihydro-α-terpineol (XXVIII) with subsequent isomerisation to (XXIX).[14,19]

The conversion of limonene (dipentene) and menth-3-ene into menthols was effected by different paths. Menth-3-ene (XXVII) is converted into the oxide (XXX) the isomerisation of which leads to menthones (XXXI), and subsequent hydrogenation gives a mixture of menthols (XXXII).[19]



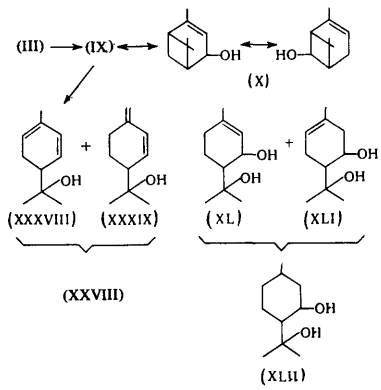
Bain and Webb converted menth-3-ene (XXVII) into 5-chloromenth-3-ene (XXXIII), hydrolysis of which gave *trans*-menth-3-en-5-ol (XXXIV). The last is readily hydrogenated into isomenthol, which can be isomerised into menthol if the temperature and duration of the reaction are sufficient[20].

The oxidation of limonene (dipentene) (XXVI) followed by reduction of the hydroperoxide leads to *p*-mentha-1,4(8)-dien-3-ol (XXXV). The oxidation of carbomenthene (XXXVI)—obtained by selective hydrogenation of dipentene—leads, after reduction, to piperitols (XXXVII), which are then hydrogenated to menthols (XXXII).

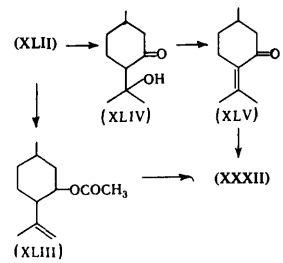
The reduction of hydroperoxides can be brought about by sodium sulphite solution, by the action of triphenylphosphine, or by alkali metal tetrahydroaluminates. The selective hydrogenation of *p*-mentha-1,8-dien-4-ol, obtainable from the hydroperoxides formed in the photosensitised oxidation of limonene (dipentene), leads to terpin-1-en-4-ol (XXII).[21]

The decyclisation of pin-3-en-2-ols (IX) and verbenols (X) takes place just like the decyclisation of α-pinene (III) but in addition a considerable proportion of *o*-mentha-4,6-dien-8-ol is formed. α- and β-8-hydroxyphellandrenes (XXXVIII) and (XXXIX), *p*-menth-1-ene-3,8- and 5,8-diols (XL) and (XLI) and 8-hydroxy-*p*-cymol are obtained predominantly. Decyclisation is brought about by the action of boiling water in the presence of aqueous solutions of zinc chloride, sodium hydrosulphite, and phosphoric acid.

8-Hydroxyphellandrenes (XXXVIII) and (XXXIX) can be converted into dehydro-α-terpineol (XXVIII) and diols into *p*-menthane-3,8-diol, that is, the menthoglycols (XLII).



The latter can be converted into cyclic acetals, which are of interest for perfumery. Reactions with acetic anhydride allow these diols to be converted into acetates of isopulegols (XLIII), from which menthols (XXXII) can be obtained. It is also possible to oxidise these diols to 8-hydroxymenthone (XLIV) which is dehydrated to pulegone (XLV) and hydrated to menthols (XXXII).



Pin-3-en-2-ols (IX) can be converted into pinan-2-ols (XVII), from which α-terpineol (II) was obtained by boiling with water[22].

Pin-3-en-2-ols (IX) and verbenols (X) are converted into verbenyl chlorides and then into verbenyl amines. By hydrolysis of the latter by Bain and Polland's method[23], the corresponding alcohols are obtained, hydrogenation of which leads to menthol.

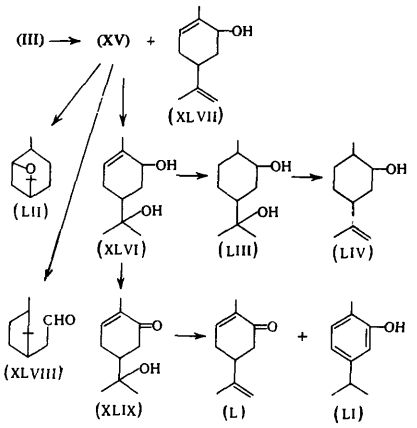
The conversion of α-pinene oxide (XV) into sobrerol or pinol hydrate (XLVI) has long been known. Klein[24], who treated α-pinene oxide (XV) with water or weak alkali solutions in the presence of an antioxidant, obtained predominantly *trans*-sobrerol (XLVI) with the impurity *p*-cymol and other hydrocarbons, and also carveols (XLVII), campholene aldehyde (XLVIII), and *p*-mentha-1,4(8)-dien-6-ol.

This method was perfected by Durbataki and Linder[25], who obtained sobrerol in quantitative yield by acting on α-pinene oxide (XV) with water saturated with carbon dioxide at 30–35°C.

Sobrerols (XLVI) can be oxidised to 8-hydroxycarbone (XLIX), dehydration of which leads to a mixture of carbone (L) and carvacrol (LI).

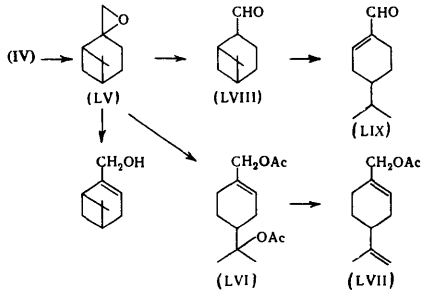
In the usual dehydration of sobrerol the products are pinol (LII) and *p*-cymol, and pyrolysis of pinol diesters gives the esters of carveol (XLVII) in good yield[26]. Thus in the pyrolysis of the diacetates at 162–205°C, 60% of a mixture of acetates of *cis*- and *trans*-carveol is obtained

together with *p*-cymol, *p*-mentha-1,5(8)-diene, pinol, and other products[27].

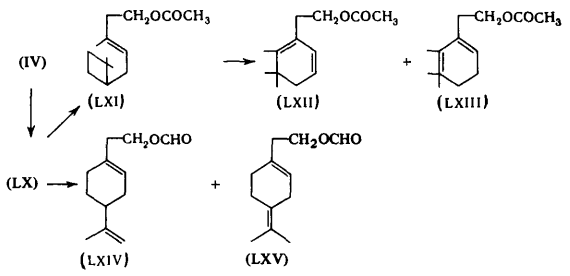


The diacetates of the dihydrosobrerols (LIII) give the acetates of dihydrocarveols (LIV). In this the dihydrocarveols retain the configuration of the dihydrosobrerols, whereas the carveols are racemised.

On treatment with a mixture of acetic acid and acetic anhydride, β-pinene oxide (LV) forms the diacetate of 7,8-dihydroxycarbomenthene (LVI), pyrolysis of which leads to perillyl acetate (LVII), *trans*-myrtanal (LVIII), and phellandral (LIX).[28] Faidutti[29] and Arbuzov[30] obtained myrtanal (LVIII) by treating β-pinene oxide (LV) with zinc chloride, as did Kergomard and Philibert-Bigou[31]. The latter, on using aluminium oxide, obtained a mixture of myrtanal, phellandral, and myrtenol (XIII), free from perillyl alcohol (LXXXV).



Nopol (LX) is an alcohol obtained by the reaction of β-pinene with formaldehyde[14]. Pyrolysis of nopol acetate (LXI) leads to a mixture of α- and β-pyronenecarbinol acetates (LXII) and (LXIII);[32] the treatment of nopol with formic acid gives homoperillyl formate (LXIV) and its isomer (LXV), a mixture of which is used in perfumery.

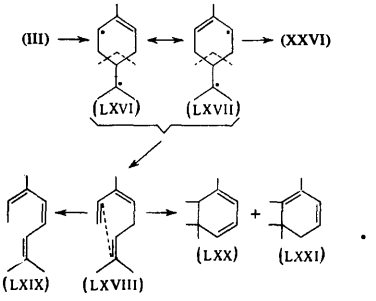


4. Radical Decyclisation

Let us examine reactions associated with the radical decyclisation of pinenes and some of their derivatives: pinanes, pinenols, verbenols, pinanols, verbanols, myrtanols, and epoxypinanes. The main aim of the decyclisation method is the production of aliphatic terpenoids.

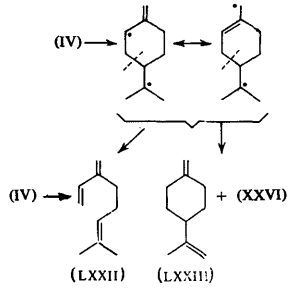
Isomerisation takes place by a radical mechanism[28,33]. Initially, the biradicals (LXVII) and (LXVI) are formed. Their peculiarity is that one of the unpaired electrons participates in the resonance structure of a hybrid of the allyl type, which determines the energy, kinetics, and structure of the products obtainable. The formation of dipentene (XXVI) from the optically active α-pinenes and of limonene from β-pinenes was explained by Burwell[34], starting from the possibility of the migration of hydrogen, which was established by molecular models.

In the decyclisation of α-pinene, in addition to dipentene (XXVI)[35,36], β-ocimenes (LXVIII) are formed, which on the one hand are isomerised into allo-ocimenes (LXIX) and on the other, are cyclised into α- and β-pyronenes (LXX) and (LXXI)[37-46]. However, it was found possible to limit these isomerisations and obtain β-ocimenes (LXVIII) in good yield:

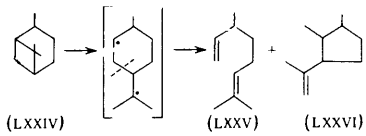


The pyrolysis of α-pinene (III) at 400–450°C leads to the formation predominantly of dipentene (XXVI); at a higher temperature, allo-ocimenes (LXIX)[47] are formed. For the production of β-ocimene (LXVIII) the time of heating had to be shortened to a few milliseconds. Blackmore effected this by using a spiral heated to 500–700°C immersed in the product heated to 50–70°C. The reaction is carried out in a flow system. The α-pinene separated by distillation is returned to the reaction zone. Under these conditions β-ocimene could be obtained in 43–47% yield calculated on the α-pinene (III) used[48,49]. Rectification of the commercial product gave a fraction with 80% ocimenes and 20% dipentene, which was used as such in many syntheses.

β-Myrcene (LXXII), limonene (XXVI), *p*-mentha-1,7(8)-diene (LXXIII), and *p*-cymene are formed in the decyclisation of β-pinene (IV)[50-52]. Myrcene can be isolated from the pyrolysate by rectification, but it is usually considered more economical to use the fraction containing 65–85% myrcene. The impurities are β-pinene, limonene, and—on long storage—camphorenes.



Thermal isomerisation of the pinanes (LXXIV) leads to 2,6-dimethylocta-2,7-diene (LXXV) with retention of the optical activity. The reaction occurs at 550–600°C, predominantly using the *cis*-pinane. The degree of conversion reaches 86%, the yield of dimethyloctadiene 64%. As a result of the cyclisation of dimethyloctadiene, irid-8-enes (LXXVI) are formed[53]:



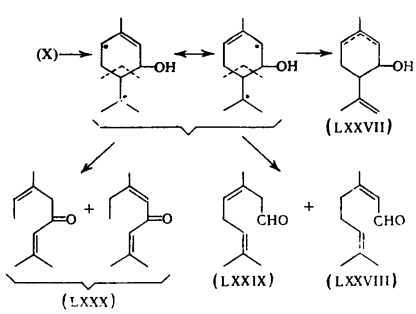
For a certain period myrcene (LXXII) was used for making the β-ocimenes (LXVIII). The isomerisation was effected with good yield in the presence of catalysts—rhodium, iridium, and their chlorides. The reaction proceeds in the presence of 0.5–2% hydrochloric acid at 80–110°C in an inert atmosphere[54]. The same method can be used to convert 2,6-dimethylocta-2,7-diene into 2,6-dimethylocta-2,6-diene and myrcenol into ocimenol.

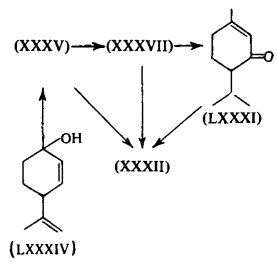
The pyrolysis of verbenols (X)—allyl isomers of pin-3-en-2-ol (IX)—leads to the formation of isopiperitenols and limonenols (LXXVII) and various aliphatic products: citrals (LXXVIII), isocitrals (LXXIX), pseudotagetones (LXXX), and also 2,2,4-trimethylcyclohex-4-enylformaldehyde[55].

The stereochemistry of these reactions is of great importance for the synthesis of (−)-menthol. (−)-α-Pinene (III) gives (−)-*trans*-verbenol with (+)-*cis*-verbenol impurity. Decyclisation of these verbenols leads to menthadienols with the same sign. A mixture of dextrorotatory menthadienols leads to (−)-menthol through the intermediate formation of (+)-neo-menthol, whereas the laevorotatory menthadienols give (+)-menthol through (+)-isomenthol. When special precautions are taken the product will contain a considerable proportion of racemic menthol. To avoid this, the production of (−)-menthol through piperitols was studied[56]. Actually, a mixture of *cis*- and *trans*-piperitols can be isomerised into (+)-*cis*-piperitol by the action of formic acid.

(−)-*trans*-Piperitenol (XXXV), obtainable from (−)-α-pinene, yields (−)-*trans*-piperitol (XXXVII), which is converted into (+)-*cis*-piperitol; the latter is isolated by distillation, then hydrogenated to (+) neo-menthol, which isomerises into (−)-menthol (XXXII). (+)-*trans*-Isopiperitenol leads to (+)-*trans*-piperitol, which is hydrogenated into (+)-isomenthol and isomerised into (−)-menthol.

Instead of this, *cis*- and *trans*-piperitols can be separated by oxidising their mixture to (−)-piperitone (LXXXI), by hydrogenation of which (+)-isomenthone is obtained and from this (−)-menthol (XXXII).





In the pyrolysis of ethers of verbenols, in addition to the esters of isopiperitenols and limonenols a significant proportion of ethers of pseudoverbenols (chrysanthenols) is formed[20]. The ethers can be readily converted into formates or hydrolysed by prolonged boiling with water. The hydrolysis of isopiperitenols leads to the formation of their allyl isomers: *cis*- and *trans*-paramentha-2,8-dien-1-ols. These are separated by fractional distillation and each of them can be converted into a mixture of *cis*- and *trans*-isopiperitenols. All these conversions proceed with retention of the optical activity.

The pyrolysis of verbanols (LXXXII) at 350–700°C leads to 2,6-dimethylocta-2,7-dien-4-ol (LXXXIII)[7,57]. At 450°C 26% of this alcohol is formed together with 19% of an acyclic aldehyde and 20% of an alcohol, which can be oxidised to tagetone and irid-8-en-4-ol (LXXXIV), which is evidently formed in the cyclisation of the alcohol (LXXXIII).

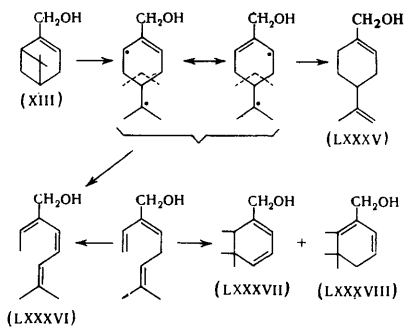
It is interesting to note that in the hydrogenolysis of a mixture of isoverbanol and neoisoverbanol over copper chromite considerable amounts of *o*-menthols are obtained[7].

The pyrolysis of verbanols leads to *cis*-*o*-menth-8-en-3-one, together with other carbonyl compounds[58].

The production of citrals and isocitrals from isopiperitenols and limonenols in an analogous manner to the production of citronellal from isopulegols was effected 40 years ago by Grignard and Doeuvre[59]. The citrals and isocitrals are readily separated by distillation, or a mixture of aldehydes and acetone is condensed in the presence of alkali and pseudoionones are obtained[60].

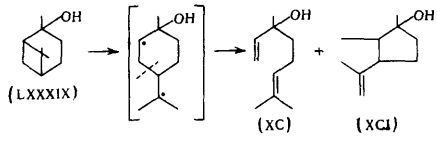
The pyrolysis of myrtenol (XIII) gives ~ 36% perillyl alcohol (LXXXV), 15% 2-methylocta-2,4,6-triene-6-carbinol (LXXXVI) and α- and β-pyronenols (LXXXVII) and (LXXXVIII)[61].

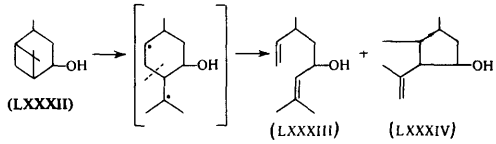
A mixture of *cis*- and *trans*-myrtenols is readily obtained from β-pinene by hydroboronation with subsequent oxidation[62] or by using aluminium alkyls[63]. By the pyrolysis of myrtanols in the vapour phase, Lemberg[64,65] obtained a mixture of 2-methylocta-2,7-dien-6-carbinol and 2-methylocta-2,7-dien-4-carbinol, which are readily separated by fractional distillation



The pyrolysis of pinanols (LXXXIX) is of great interest, since it leads to linalool (XC). Pinanols can be obtained by the hydrogenation of pin-3-en-2-ols (IX) or by starting

from hydroperoxides of pinanes. Pyrolysis is carried out at 600°C in a flow system in the absence of Lewis acids, which bring about dehydration. As a result of the cyclisation of linalool, plinols (XCI) are formed and also 2,6-dimethylocta-2,7-dien-4-ol, 3-ethyl-2,3-dimethyl-cyclobutyl methyl ketone, and α-terpineol (II). *cis*-Pinanol gives 95% linalool *trans*-pinanol 75%. (+)-*cis*- and (−)-*trans*-pinanol corresponds to (−)-linalool, (−)-*cis*- and (+)-*trans*-pinanol to (+)-linalool[66,67]. The cyclisation of linalool at 650°C leads to the formation of four stereoisomeric plinols[68].





cis-Dihydronopol, readily obtained by the catalytic hydrogenation of nopol (LX), forms, after pyrolysis at 500–600°C, a mixture containing 50% 2-methyl-6-vinyloctan-8-ol. Partial hydrogenation of this alcohol at the vinyl group gives homocitronellol (6-ethyl-2-methyloctan-8-ol).[69]

5. Conversions of Aliphatic Hydrocarbons

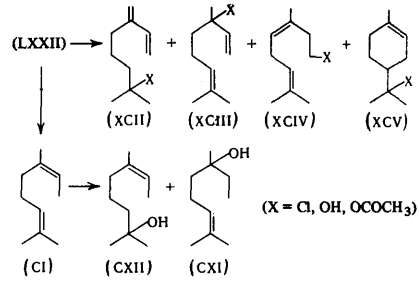
The production of almost unlimited amounts of β-myrcene (LXXII), β-ocimene (LXVIII), allo-ocimenes, and products of their partial hydrogenation, namely, 2,6-dimethylocta-2,7-diene made possible a large number of syntheses of commercial interest.

The main reactions of these hydrocarbons are as follows: (1) the addition of organic acids for the production of esters (the Bertram–Wallbaum reaction): (2) the oxidation of double bonds with subsequent isomerisation to aldehydes or ketones or hydrogenation to alcohols; (3) the production of organometallic derivatives with subsequent conversion into alcohols; (4) the addition of halogens, hydrogen halides or hypohalogen acids with subsequent pyrolysis of the hydrohalides, dehydration of the halogenohydrins to unsaturated halogen derivatives or dehydrohalogenation to epoxides; the hydrolysis of halides to alcohols or conversion into esters by reaction with salts or organic acids.

In incomplete addition, the double bonds compete with one another. In instances when it is possible allyl rearrangements take place.

Syntheses from β-myrcene (LXXII) have most value. In this way above all linalool (XC), geraniol, nerol, and their esters are obtained.

β-Myrcene is converted into the monochlorides (XCII)–(XCV). Without a catalyst the predominant products are the chlorides of myrcenol, terpineol, and borneol. The amount of these chlorides, especially myrcenyl chlorides, can be decreased by carrying out the hydrochlorination at low temperature in



the presence of an antioxidant and a catalyst—copper or a copper(I) salt[70]. The addition of hydrochloric or hydrobromic acid is controlled spectrometrically by the disappearance of the conjugated double bond. Increase in temperature and increase in the amount of catalyst decreases the proportion of linalyl chloride and increases the content of geranyl and neryl chlorides. Under optimal conditions the final concentration of myrcenyl chloride < 10%; without a catalyst, its concentration reaches 50–60%.[71] Conversion of the halides into esters in the absence of a catalyst does not give good results. The catalysts used can be bases containing nitrogen or phosphorus[72–74], for example, trimethylamine, triethanolamine, phosphonium salts or derivatives of phosphorus(III) (phosphines) capable of forming quaternary derivatives in the presence of alkyl halides, or even phosphorus[74]. The reaction proceeds in an acid medium, for example, in the presence of acetic acid, which facilitates the formation of esters of linalool[75] or in the presence of bases, which increases the yields of esters of geraniol and nerol. The use of solvents to facilitate the rearrangement is recommended, and dilute dimethyl sulphoxide is also used[73]. The yield of acetates can reach 75–95%.

To diminish the formation of myrcenyl chloride dihydrochlorination of myrcene is carried out[76,77]. This reaction was effected at 10–50°C in the presence of copper chloride. The conversion into the ester was performed in the presence of a base, for example, 1% trimethylamine. The formation of geranyl acetate and neryl acetate is facilitated by raising the temperature and increasing the duration of reaction. ~ 50% of the α-isomers are formed.

Good results were obtained in the hydrolysis of products of the addition of two molecules of hydrochloric acid[78,79]. The reaction was brought about by using an aqueous suspension of calcium carbonate in the presence of an emulsifier. In this way 2-hydroxy-2,3-dihydro-linalool, -geraniol, and -nerol were obtained. 2,3-dihydro-2-hydroxylinalool can be converted into isomers by the action of formic acid, with a yield of 73–75%. The dehydration of glycols leads to a mixture of isomers of α- and β-linalool, geraniol, and nerol. Carrying out the dehydration without appropriate precautions leads to the production of ocimenol and α-ocimenes. The production of β-ocimene from α-pinene in good yield allows β-myrcene to be replaced by this terpene.

The mixture of chlorides obtained in monohydrochlorination, which contains geraniol and neryl chlorides can be converted into citrals by the Kröhnke procedure with the

Liebermann method[80]. Pseudoionones are obtained by reaction in a medium of acetone.

The production of geraniol and nerol from pinenes made possible the synthesis of citral. It is difficult to carrv out the catalytic dehydrogenation in a directed manner. In the presence of copper catalysts disproportionation occurs, leading to the production of citronellal[81,82]. The oxidation of geraniol and nerol with chromic acid leads to citral in 80–85% yield. It gives better results than oxidation with manganese dioxide (68%) or by functional exchange[83,84]. The Openhauer reaction with aluminium alkoxides in an acetone medium leads to pseudoionones[85–89].

Whereas the oxidation of 2,3-dihydro-2-hydroxylinalool gives only 44–47% 2,3-dihydro-2-hydroxycitral, which is more readily hydrogenated to 2,3-dihydro-2-hydroxycitronellal than dehydrogenated to citral, 2,3-dihydro-2-hydroxygeraniol and -nerol can be converted over copper chromite directly into hydrohydroxycitronellal in 90–95% yield[90,91].

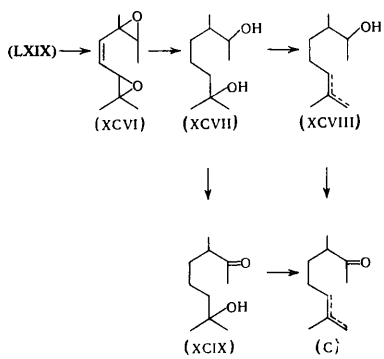
Ocimenol can be obtained from β-myrcene through the intermediate formation of a sulphone obtainable by the action of sulphur dioxide at 50–100°C. The sulphone is hydrated by 40–60% sulphuric acid and the hydrate decomposed by heating to 120–170°C.[92] The decomposition can also be brought about in the presence of 1–2% amine, for example, triethanolamine, or calcium carbonate.

By the action of hydrochloric acid at 20–110°C myrcenol and ocimenol are converted into a mixture of 2,6,6-trimethyl-2-vinyltetrahydropyran and 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran, used in perfumery.

2-Methylmethylene-6-oct-2-en-8-ol was obtained in 68% yield from β-myrcene by the action of di-isopentylborane (obtained by the reaction of boron hydrides with 2-methylbut-2-ene). This alcohol is readily hydrogenated to citronellol[93].

The monoepoxidation of β-myrcene to β-ocimenes takes place at the double bond in the 2,3-position. Isomerisation of monoepoxides under the action of acids[94] leads to 2,6-dimethylocta-4,6-dien-3-ols.

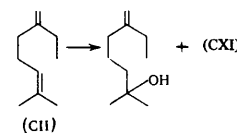
Allo-ocimenes can be used for very interesting syntheses. The polymeric peroxide which is formed on adding oxygen yields the diepoxide (XCVI) on heating; the structure of this was the subject of discussion[95–100]. This diepoxide is readily hydrogenated into *erythro*- and *threo*-2,6-dimethyloctane-2,7-diol (XCVII), partial dehydration of which gives a mixture of the *erythro*- and *threo*-isomers of the α- and β-elgenols (XCVIII), already known under the name of secondary citronellols. The pyrolysis of the diacetates of these glycols leads to acetates of α-elgenol. Oxidation of the glycols with chromic acid leads to hydroxyelgenol (XCIX), which is dehydrated into a mixture of α- and β-elgenols (C).



Theimer[101] hydrochlorinated allo-ocimenes in a flow system. Treatment of the chlorides with water in the presence of an emulsifier leads to a mixture of the alcohols 2,6-dimethylocta-3,5-dien-2-ols and 2,6-dimethylocta-2,4-dien-6-ols. Hydrogenation of this mixture gives the more stable saturated alcohols.

The syntheses starting from 2,6-dimethylocta-2,7-diene (LXXV), obtainable in the pyrolysis of pinane (LXXIV) or by partial hydrogenation of myrcene (LXXII), are of great interest.

The product of the pyrolysis of pinanes is optically active. It includes irid-8-enes (LXXVI)[102,103]. The partial hydrogenation of myrcene (LXXII) is insufficiently selective[104] and the product obtained contains 2,6-dimethylocta-2,6-diene (CI) and 2-methyl-6-methyleneoct-2-ene (CII).



2,6-Dimethylocta-2,7-diene (LXXV) can be converted into β-citronellol (CIII) through organoaluminium compounds by the action of lithium tetrahydroaluminate, or better tri-isobutylaluminium. The organometallic compound is oxidised by moist air and the aluminate formed is hydrolysed to citronellol[99,105–108]. The yield reaches 77%.

In another variant of this synthesis diborane converts 2,6-dimethylocta-2,7-diene (LXXV) into tricitronellylboron[109]; the latter is oxidised to citronellyl borate, from which β-citronellol (CIII) is also obtained by hydrolysis or oxidative hydrolysis with hydrogen peroxide[91,109]. This method, like the method via tricitronellylaluminium, was perfected by carrying out the oxidation in the presence of organo-zinc or -cadmium compounds. The yield is 80%.[110]

(−)-Citronellol is obtained from (+)-α-pinene (III) through the intermediate formation of (+)-dimethyloctadiene, and (+)-citronellol from (−)-α- and (−)-β-pinenes through (−)-dimethyloctadiene[111].

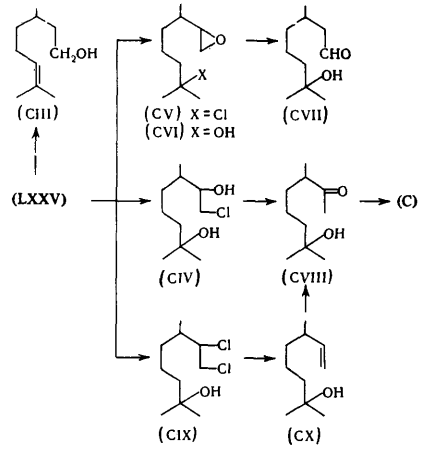
The optically active citronellols prepared in this way can rival the (+)-citronellol obtained by the hydrogenation over Raney cobalt of geraniol and nerol synthesised from α-myrcene and ocimene[112].

There are other methods of obtaining hydrohydroxycitronellol and the corresponding aldehyde, and also elgenol from 2,6-dimethylocta-2,7-diene.

The following schemes are given in Webb's patents[113,114].

A hydrocarbon (LXXV) is converted into 2-chloro-2,6-dimethyloct-7-ene, from which by the action of peracetic acid or through the chlorohydrin (CIV) the epoxychloride (CV) is obtained, hydrolysis of which by an aqueous suspension of $Ca(OH)_2$ gives 7,8-epoxy-2,6-dimethyloctan-2-ol (CVI) in good yield.

Pyrolysis of this product at 250°C leads to hydrohydroxycitronellal (CVII), which can also be obtained through the chlorohydrin. After treatment with lime at 200–210°C a mixture of products is formed, from which via the hydrogen sulphite compound a hydroxycitronellal containing 5–8% α-citronellal is isolated. On boiling the non-aldehyde fraction with sodium in isopropanol it is converted into 2,6-dimethyloct-7-en-2-ol, which can be used for the production of the epoxide (CVI).



In the conversion of the chlorohydrin (CIV) into the epoxide (CVI) a certain proportion of 2,3-dihydro-2-hydroxyelgenone (CVIII) is formed, from which α- and β-elgenones (C) can be obtained.

7,8-Dichloro-2,6-dimethyloctan-2-ol is isolated as an intermediate in the production of the chlorohydrin (CIX). After treatment with potassium hydroxide at 200°C in ethylene glycol, the allene 2,6-dimethylocta-6,7-dien-2-ol is obtained; by catalytic hydrogenation or by reduction with sodium in t-butanol it is converted into 2,6-dimethyloct-7-en-2-ol (CX), which is used again. Under the action of mercury sulphate in sulphuric acid the allene derivative forms hydrohydroxyelgenone (CVIII).

Webb also described[115] the hydrogenation of 7,8-epoxy-2,6-dimethyloctan-2-ol (CVI) to hydrohydroxycitronellol, which on passage over copper chromite forms hydrohydroxycitronellal (CVII) and α-citronellal. It can also be dehydrogenated into a mixture of α- and β-citronellals.

Under the action of hydrobromic acid after Karasch, 2,6-dimethylocta-2,7-diene and 2-chloro-2,6-dimethyloct-7-ene add on hydrogen bromide contrary to the Markovnikov rule. 2,8-Dibromo-2,6-dimethyloctane and 2-chloro-8-bromo-2,6-dimethyloctane are formed, by hydrolysis of which hydrohydroxycitronellol is obtained, which can be dehydrated to a mixture of α- and β-citronellols.

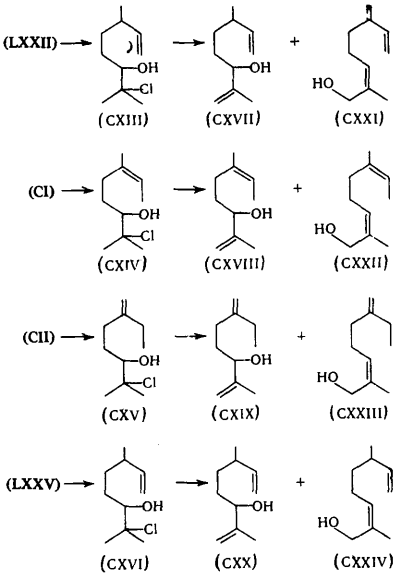
Pyrolysis of the dihalogenides leads to mixtures of the bromides of α- and β-citronellols, with the former predominating.

The production of optically active citronellals from (−)-2,6-dimethylocta-2,7-diene allows (−)-menthol to be synthesised.

We will pay some attention to the production of α-citronellol and α-citronellal free from ester oils and having a more pleasant odour than their β-isomers. It has long been known that α-citronellal is obtained by the dehydration of hydrohydroxycitronellal. It is found among the side-products in the production of hydrohydroxycitronellal by hydration of the hydrogen sulphite compound of β-citronellal. It is also known that its cyclisation into isopulegol is slower than the isomerisation of the β-isomer[7,60,116]. In the production of citral from hydrohydroxygeraniol and nerol, α-citral is formed, the odour of which, however, was not better than that of β-citral.

Partial hydrogenation of β-myrcene (LXXII) leads to not only 2,6-dimethylocta-2,7-diene (LXXV), as already stated, but also to 2,6-dimethylocta-2,6-diene (CI) and to 2-methyl-6-methyleneoct-2-ene (CII). Hydrogenation of β-ocimene (LXVIII) leads mainly to 2,6-dimethylocta-2,6-diene (CI), and hydrogenation of allo-ocimene to 2,6-dimethylocta-2,4-diene.

By the action of hydrochloric acid on 2,6-dimethylocta-2,6-diene (CI) Kitchens[117] obtained dihydrolinalyl chloride, which he hydrolysed to dihydrolinalool (CXI). In this the formation of dihydromyrcenol (CXII) was not noted. On the other hand, Webb succeeded in adding halogen to the second carbon atom of various dihydroterpenes mentioned earlier. The chlorohydrins (CXIII), (CXIV), (CXV), and (CXVI) were obtained by the addition of hypochlorous acid to myrcene (LXXII)[76]. When these products were hydrolysed and the resulting tertiary alcohol was dehydrated, the secondary alcohols (CXVII), (CXVIII), (CXIX), and (CXX), and their allyl isomers (CXXI), (CXXII), (CXXIII), and (CXXIV) were obtained.



The addition of organic acids by the Bertram–Walbaum reaction[118] takes place at the 2,3-double bond. The reaction occurs at 15° and 45°C in the presence of 1–4 parts organic acid containing 0.25–1% sulphuric acid. By replacing the latter by an acid ion-exchange resin, the reaction could be carried out continuously.

The addition of formaldehyde to β-myrcene leads, according to Sommerwell, to a mixture of 3-(4-methylpent-3-enyl)-5,6-dihydropyran and 4-(4-methylpent-3-enyl)-5,6-dihydropyran which can be converted into alcohols and their esters. On carrying out condensation in an organic acid an ester of 2-methyl-6-methyleneocta-1,7-diene-carbinol is also formed.

Webb studied the addition of formaldehyde to dihydroterpenes obtained by partial hydrogenation of β-myrcene and β-ocimene[49]. Heating is necessary, at least to 240°C, better 250–285°C. In the presence of an organic acid a lower temperature is used, for example, 130–160°C in acetic acid. Primary alcohols or their esters are obtained in this way. The alcohols can be converted into aldehydes. According to Webb's results the addition of carbinol takes place at the third carbon atom.

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Hence the development of the chemistry of the pinenes, connected with the use of decyclisation has created a serious basis for the production of many important synthetic perfumes.

The following have been obtained:

1. Aliphatic terpene alcohols and their esters: linalool, geraniol, nerol, α- and β-citronellols, α- and β-elgenols.

2. Aldehydes and ketones and their derivatives: citral, pseudoionones, α- and β-citronellal, hydrohydroxycitronellal, α- and β-elgenones.

3. Monocyclic terpene alcohols: carveols, dihydrocarveol, isopiperitenols, piperitenols, isopulegols, menthols, and the corresponding ketones and aldehydes.

The industrial production of linalool, citral and pseudoionones on a large scale based on pinenes, together with the synthesis of these substances from acetylene made it possible to get rid of the inconvenience due to the instability, the difficulty of acquiring, and the variations in price of the essential oils which were for long the sole source of production of these materials. Synthetic perfumes are obtained at a lower price and with a greater purity than previously from the essential oils. This assists the development of the perfumery industry, especially for the production of mass perfumery. The synthetic products are used to reconstruct many essential oils. Some success was achieved, thanks to carrying out planned and unremitting investigations. It should be noted, however, that the results of these studies are still in the state of being used by only a few powerful industrial groups which produce these products in amounts ranging from a few hundreds to 1000–2000 tonnes per year.

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Dimerisation of Alkenes

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This review discusses published work on catalysts, reaction conditions, composition of products, and mechanism, relating to the dimerisation of alkenes. It is shown that dimerisation is a very important practical method of synthesis of higher alkenes of various structures. The relationship between the type of catalyst activity and the course of the reaction is demonstrated in the specific case of the dimerisation of propene. An analysis of the activity and selectivity of catalysts is given, and the effectiveness of various methods of dimerisation is assessed from the point of view of their industrial exploitation. The most detailed discussion is given to the literature on the dimerisation of alkenes under the influence of complex organometallic catalysts, which have a very high activity. The major areas of application of dimers as intermediates in petrochemical and general organic synthesis are indicated. 139 references.

CONTENTS

1. Introduction 789
2. Dimerisation catalysts for alkenes 789
3. Dimerisation of ethylene 790
4. Dimerisation of propene 791
5. Dimerisation of butenes and higher alkenes 794
6. Codimerisation of alkenes 794

1. INTRODUCTION

Dimerisation of alkenes, unlike polymerisation, is a relatively new area of industrial organic synthesis, developed during the past decade. Previously, liquid polymers of ethylene, propene, and butenes were of relatively limited interest in the production of motor fuel constituents, lubricants, and some synthetic detergents (for example, dodecylbenzenesulphonates). The impetus for the deployment of effort in this direction was provided by Ziegler's discovery in 1952 of the selective dimerisation of alkenes by organoaluminium compounds, which demonstrated the possibility of synthesising individual higher alkenes of known structure. Ziegler's method was quickly adopted in three areas of practical importance: the preparation of but-1-ene by the dimerisation of ethylene, the synthesis of isoprene from propene, and the production of higher alkenes and primary alcohols with a linear carbon chain. The search for new dimerisation catalysts for alkenes was stimulated by a large number of papers on the use of C_4–C_6 alkenes as the starting products in dehydrogenation, oxidation, polymerisation, hydration, and other reactions. Progress in this area would obviously have been impossible but for the development of gas–liquid chromatography, infrared spectroscopy, and nuclear magnetic resonance as standard methods of analysis and identification of alkenes.

Many patents on the dimerisation of alkenes have appeared in recent years, as well as many papers on the mechanism of this reaction under the influence of various catalysts. However, a systematic review of the literature in this area has not yet been attempted: to the best of our knowledge, the present article is the first review of this subject. We shall not attempt to deal exhaustively with the existing literature, but we shall examine instead the correlation between the course of the reaction and the type of activity of the catalysts. The analysis will be made in the specific case of the dimerisation of propene, mainly because of the great practical importance of this reaction at the present time.

2. DIMERISATION CATALYSTS FOR ALKENES

A large number of dimerisation catalysts for alkenes, differing in the composition of the products and in the reaction conditions, has been described. In particular, the use of acidic catalysts for the preparation of liquid polymers (including dimers) of propene and isobutene[1,2] for use as motor fuel constituents and in the synthesis of detergents is well known. Ethylene does not dimerise under the influence of acidic catalysts. With propene, the primary dimerisation products undergo side reactions (polymerisation, isomerisation, disproportionation, etc.[3]). Hence the yield of the dimer of propene is small, and its isomeric composition is quite complex; we are therefore justified in concluding that acidic catalysts are unsatisfactory for the selective dimerisation of propene[4]. However, work on improving the selectivity of acidic catalysts is continuing, and will be discussed below.

Selective dimerisation of ethylene was first achieved with a cobalt catalyst[5]. Schultz and coworkers[6,7] have recently made a detailed study of the dimerisation of various alkenes on catalysts of this type. The main disadvantage of catalysts based on cobalt oxide is their relatively low activity, which limits the prospects of their industrial application.

The dimerisation of propene by finely dispersed potassium in a hydrocarbon medium[8] was reported in 1961. In spite of the low activity of the catalyst and of the stringent conditions of the reaction, the process has undergone considerable development in connection with the production of 4-methylpent-1-ene, an important monomer and intermediate in industrial organic synthesis.

The dimerisation of alkenes by Ziegler's method with alkylaluminium catalysts[9] offers the greatest practical interest at present. Thus, the dimerisation of propene in the presence of tripropylaluminium is the basis of an industrial method of preparation of isoprene from propene[10,11]. A process for the codimerisation of ethylene and propene to give 2-methylbut-1-ene, followed by dehydrogenation to

isoprene, has been developed[12]. The dimerisation of ethylene in the presence of triethylaluminium gives very pure but-1-ene, used in the production of high-quality polymeric products[13].

The dimerisation of alkenes under the influence of complex organometallic catalysts proceeds under mild conditions and with high yields of product. In 1961 a method of oligomerisation of ethylene with homogeneous catalytic systems of the Ziegler type was proposed in the U.S.A., based on alkylaluminium halides and nickel compounds[14], and in 1963 a method of dimerisation of propene was proposed in the U.S.S.R. using catalysts of very similar composition, as well as a method for the production of dienes by means of these catalysts[15-17]. The dimerisation of propene by alkylaluminium halides in conjunction with organic nickel salts has also been patented by the Shell Company[18].

The first reports of the dimerisation of alkenes by complex Ziegler catalysts were published almost simultaneously in West Germany[19,20], France[21], and the U.S.S.R.[22-24]. Ewers[19] used a highly active homogeneous catalyst prepared by treating nickel acetylacetonate, bis-(π-allyl)nickel, or π-allylnickel chloride with a dialkylaluminium chloride in a toluene medium. A paper by Wilke and coworkers[20] describes the dimerisation of ethylene and propene under the influence of π-allylnickel chloride in conjunction with Lewis acids and tertiary phosphines. Chauvin and coworkers[21] used the catalytic system nickel acetylacetonate–ethylaluminium dichloride. Complex dimerisation catalysts for alkenes based on various π-complexes of nickel have been proposed[25].

The dimerisation of ethylene and propene and the codimerisation of these alkenes under the influence of catalytic systems based on alkylaluminium halides and organic nickel salts[22-24], similar to the stereospecific polymerisation catalysts for butadiene[26], is characterised by very mild conditions (room temperature and normal pressure). There is a marked difference between these catalysts and alkylaluminium catalysts containing "colloidal" nickel: the latter also are dimerisation catalysts for alkenes[27], but they require more stringent reaction conditions leading to the formation of dimers of different structure.

Thus, the dimerisation of alkenes can be achieved with catalysts of quite different type. Accordingly, a variety of dimerisation mechanisms and of structures of the resulting product are observed. The specific features of the dimerisation of various alkenes are discussed in detail below.

3. DIMERISATION OF ETHYLENE

According to Cheney and coworkers[28], ethylene dimerises on a cobalt catalyst at 40°C and 50 atm pressure with a conversion of ~ 50%, and 80% selectivity with respect to butenes. The conversion of the monomer and the composition of the dimer depend on the contact time: with an input of ethylene of 72 g per 1 litre of catalyst per hour the conversion is 74% and the main product of the reaction is but-2-ene (91%); if the input is raised to 360 g litre^{-1} h^{-1} the conversion drops to 37% and the dimer contains up to 70% of but-1-ene. Treating the carrier (activated carbon) with aqueous ammonia increases the activity of the cobalt catalyst but degrades its selectivity towards dimerisation[6,7]: the yield consists of ~ 20% butenes, 60% hexenes, and 20% high-boiling hydrocarbons. The hexene fraction consists mainly of linear alkenes. A great deal of work has been published on the dimerisation of ethylene on nickel catalysts[29-35]. The above solid dimerisation catalysts have not been exploited industrially so far because they are difficult to prepare, they have low activity and stability, and for a number of other reasons.

At the present time, the dimerisation of ethylene by homogeneous catalysis (and in particular using triethylaluminium as the catalyst) is attracting most attention. By this method[9], pure but-1-ene can be obtained with high yield by withdrawing it from the reactor as soon as it is formed or by carrying out the reaction in the presence of "colloidal" nickel[27]. The dimerisation of ethylene by Ziegler's method has been studied at the Scientific Research Institute of Synthetic Alcohols and Organic Products (NIISS)[36] and at the All-Union Scientific Research Institute of Olefins (VNIIOlefin)[37]. The purest but-1-ene is obtained at low conversions of the ethylene. Thus, it is convenient to prepare a mixture of ethylene and butene (containing up to 10% of butene) and to use it as the raw material for the production of a copolymer having good mechanical properties[37]. At higher conversions of the ethylene (20%), appreciable amounts of C_6 and C_8 alkenes are produced as well as but-1-ene.[38] Chernikova[13] studied the influence of various nickel compounds (as additives to the triethylaluminium) on the rate and selectivity of the dimerisation of ethylene. She suggests that the ethylene is activated on the surface of freshly reduced nickel, and this assists its further penetration along the aluminium–carbon bond.

Various catalytic systems for the dimerisation of alkenes based on aluminium alkyls and transition metal alkoxides have been proposed. Their activity is higher than that of the aluminium alkyls[39-42]: for example, ethylene dimerises at 50–100°C and 1–10 atm in the presence of triethylaluminium and tetrabutoxytitanium with up to 65% yield of but-1-ene[41]. The dimerisation of ethylene to but-2-ene at 0°C in the presence of the triethylaluminium–cobalt acetylacetonate catalytic system has also been reported[43].

Unlike the aluminium alkyls, alkylaluminium halides by themselves dimerise alkenes only in very low yields, even under drastic conditions[44]. However, they yield active dimerisation catalysts for ethylene in conjunction with dialkyldihalogenostannanes[45].

The most active dimerisation catalysts are prepared by treating alkylaluminium halides with nickel compounds. The use of these catalysts for the production of high-molecular-weight polyethylene was patented by Ziegler[46]. The dimerisation of ethylene under the influence of catalysts of this type has also been described in a patent[14]. The reaction was carried out in the presence of the complex of nickel carbonyl with triphenylphosphine, in conjunction with ethylaluminium sesquichloride, at 100°C and 30 atm. Subsequently, more active catalytic systems were disclosed, in which the nickel compounds were salts of organic acids, phenols, enols, or sulphonic acids, which are fairly readily soluble in hydrocarbon solvents[18]. An even more active catalyst was prepared from nickel acetylacetonate, ethylaluminium sesquichloride, and triphenylphosphine[19]: in this system, 18×10^5 moles of ethylene are dimerised in 15 min at 60°C per g-atom of nickel. The yield of butenes can be as high as 94%, with a 95% content of but-2-ene. As well as butenes, catalysis by systems of this type produces hexenes, the relative yield of ethylene dimers and trimers depending on the rate at which ethylene is passed through the catalyst solution[22].

Obviously, the chlorides of the platinum group metals and their complexes with alkenes[47-50] cannot find extensive practical application as dimerisation catalysts for alkenes because they are too expensive as well as being insuffici-

ently active. Palladium chloride dimerises ethylene with up to 90% selectivity at 20–70°C and 1–40 atm.[50] The yield of butenes is found to be very sensitive to the nature of the solvent[50]. A Dutch patent[48] recommends the use of a nitro-compound as the medium for this reaction. It has been suggested[50] that palladium chloride initiates the dimerisation in the presence of hydrogen chloride by a mechanism analogous to that of the Friedel–Crafts catalysts:

$$CH_2{=}CH_2 \xrightarrow[HCl]{PdCl_2} CH_3CH_2^+\,PdCl_3^- \xrightarrow{CH_2=CH_2}$$

$$\rightarrow (CH_3CH_2CH_2CH_2)^+\,PdCl_3^- \rightarrow (CH_3CH_2\overset{+}{C}HCH_3)\,PdCl_3^- \rightarrow CH_3CH{=}CHCH_3 + PdCl_2 + HCl$$

Rhodium chloride is active in the dimerisation of ethylene at 30–50°C, whereas ruthenium chloride requires a higher temperature[51].

Cramer[52] made a detailed study of the dimerisation of ethylene under the influence of rhodium chloride in alcoholic HCl solutions, and proposed the following mechanism for the reaction:

$$\begin{array}{lcl} Rh^{III}Cl_3\cdot 3H_2O & & C_2H_4 + [C_2H_5Rh^{III}Cl_3S]^{2-} \quad (B)\\ +C_2H_4 \downarrow (1) & & +S \uparrow\downarrow -S\ (3)\\ (A)\ [Cl_3Rh^{I}(C_2H_4)_2]^- & \xrightarrow[(2)]{+H^+,\,Cl^-} & [C_2H_5Rh^{III}Cl_3(C_2H_4)S]^- \quad (C)\\ +C_2H_4 \uparrow -C_4H_8\ (6) & & +S \downarrow (4)\\ (E)\ [Cl_3Rh^{I}S(CH_3CH_2CH{=}CH_2)]^- & \xleftarrow[(5)]{-H^+,\,Cl^-} & [CH_3CH_2CH_2CH_2Rh^{III}Cl_3S_2]^- \quad (D) \end{array}$$

($S = Cl^-$, H_2O or solvent).

Activation of the catalyst (*1*) occurs by the reaction between $RhCl_3$ and ethylene with formation of a complex anion of univalent rhodium with two ethylene ligands. This is followed by fast protonation (*2*) of the complex (A) to give the ethyl derivative (B), and by addition (*4*) of a coordinated molecule of ethylene at the rhodium–carbon σ-bond (limiting step), with formation of the butyl derivative (D). The latter is rapidly converted into the complex (E) containing a butene ligand, which is rapidly replaced by ethylene, reaction (*6*). Thus, the starting complex (A) is regenerated. The author[52] introduces the ligands *S* into the formulae in order to satisfy the coordination numbers of Rh^{I} and Rh^{III} (4 and 6 respectively).

4. DIMERISATION OF PROPENE

a. Cationic Dimerisation

Catalysts of the acidic type have not gained wide acceptance in practice for the selective dimerisation of propene because of the low yields and complex composition of the dimer, due to the possibility of side reactions under the conditions of dimerisation. The reactivity of low-molecular-weight alkenes towards dimerisation under the influence of acidic catalysts increases very significantly in the series ethylene–propene–isobutene, as a result of the electronic σ,π conjugation effect. A proton (or cation) attacks the propene molecule in accordance with Markovnikov's rule:

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H^+} CH_3{-}\overset{+}{C}H{-}CH_3$$

$$CH_3{-}CH{=}CH_2 + CH_3{-}\overset{+}{C}H{-}CH_3 \rightarrow CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightarrow$$

$$\xrightarrow{-H^+} CH_3{-}\underset{CH_3}{C}H{-}CH{=}CH{-}CH_3\ .$$

The resulting intermediate isohexyl carbonium ion usually interacts rapidly with the next propene molecule to give the trimer, and so on. Also, the secondary carbonium ion is not stable[53], and easily rearranges according to the scheme

$$CH_3CH\overset{+}{C}H_2CHCH_3 \xrightarrow{-H^+} \text{4-methylpent-1-ene, 4methylpent-2-ene}$$

$$\begin{array}{l} \quad\quad\quad\

and therefore the composition of the dimerisation product depends on the exact form of the catalyst and on the reaction conditions. The choice of carrier plays an important role: in particular, its porosity should not be too high[71]. A proposed dimerisation catalyst consists of sodium or lithium, dispersed on an anhydrous potassium salt[78-81]. The dimerisation of propene by a continuous method[65] at 140°C and 100 atm, and a volume velocity of 0.7 h^{-1}, on a Na/K_2CO_3 catalyst, gives a dimer of the following composition: 4-methylpent-1-ene (85%), 4-methylpent-2-ene (7%), 2-methylpent-2-ene (0.5%), 2-methylpent-1-ene (0.5%), and n-hexenes (7%). Separation of 4-methylpent-1-ene and 4-methylpent-2-ene is difficult because the boiling points are very similar. Hence, the use of a mixture of the two isomers in the polymerisation has been suggested[71]. In a Belgian patent[65], the dimer was fractionated on a column with an efficiency of 100 theoretical plates, with a 60% take off, giving a distillate containing 99.9% of 4-methylpent-1-ene.

Using potassium on granulated magnesia as the dimerisation catalyst, the product contains 55% of 4-methylpent-1-ene, 38% of 4-methylpent-2-ene, and 7% of other hexenes[82]. Polymerisation of a mixture of alkenes of approximately this composition in the presence of $AlBr_3$ has been suggested for the preparation of a liquid polymer useful for electrical insulation and as a lubricating oil additive[83]. Alkali metals on graphite[84], active carbon[85], carbon black[86], alumina[87], magnesium silicate[88], and metal hydrides[89] catalyse the dimerisation of propene mixed with methylpentenes of various compositions. These catalysts can be regenerated by being heated to 200–300°C in a stream of hydrogen[85,86].

The dimerisation mechanism of propene in the presence of alkali metals has been investigated by Shaw and coworkers[90], who suggest that the reaction involves the formation of an organometallic compound with a strongly polar M–C bond on the catalyst surface. Partial dissociation with formation of carbanions as kinetically independent particles is possible:

$$CH_3{=}CH{-}CH_3 \xrightarrow{M} [CH_3 \cdots CH \cdots CH_3]^- M^+ .$$

The allyl carbanion attacks a propene molecule. The resulting isohexyl carbanion, unlike the allyl carbanion, is not stabilised by interaction of an unshared electron pair with the double bond. It is very reactive, and extracts a proton from the next propene molecule. The end result of these transformations is the production of 4-methylpent-1-ene and simultaneous regeneration of an allyl carbanion:

$$[CH_2{\cdots}CH{\cdots}CH_2]^- M^+ + \overset{\delta^-}{CH_2}{=}\overset{\delta^+}{CH}{-}CH_3 \longrightarrow CH_2{=}CHCH_2\underset{CH_3}{\underset{|}{C}}HCH_2\ M^+ \xrightarrow{+C_3H_6} CH_2{=}CHCH_2\underset{CH_3}{\underset{|}{C}}HCH_3 + [CH_2{\cdots}CH{\cdots}CH_2]^- M^+ .$$

Isomerisation of 4-methylpent-1-ene occurs through the formation of a carbanion with migration of an allyl proton:

$$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH{=}CH_2 + R^-M^+ \xrightarrow{-RH} \left[CH_3\underset{CH_3}{\underset{|}{C}}HCH \cdots CH \cdots CH_2\right]^- M^+ \xrightarrow{+RH} \rightarrow CH_3\underset{CH_3}{\underset{|}{C}}HCH{=}CHCH_3 + R^-M^+ .$$

The following alkali metal derivatives as well as the alkali metals themselves are used as dimerisation catalysts: hydrides[91-93], amides[94,95], and carbides[96]. The reaction conditions and the composition of the products obtained in the presence of these catalysts are about the same as when alkali metals are used. The dimerisation of propene under the influence of carbon complexes of the alkali metals has been proposed as the first stage in the synthesis of isoprene from propene[97]. A dimer containing ~ 65% of 4-methylpent-2-ene is isomerised into a mixture of 2-methylpent-2-ene and 3-methylpent-2-ene on an alumina-silica catalyst at 290°C, followed by pyrolysis at 670°C with a contact time of 0.5 s and dilution with water vapour in the molar ratio of 1 : 5.

The alkyl derivatives of alkali metals also catalyse the dimerisation of propene at temperatures between 40 and 225°C and pressures up to 250 atm.[98] Complexes of the general formula AMR_3 can also be classified with this type of catalyst, where A is an alkali metal, M is zinc, cadmium, tin, or lead, and R is hydrogen or a hydrocarbon radical[99]. Because of the low activity of these catalysts, contact times of up to 20 h are needed[99], which argues against their practical exploitation.

Thus, catalysts based on the alkali metals and their derivatives can dimerise propene, with a high yield of the desired product, but they require the application of high temperatures and pressures, and long contact times, and they are also very sensitive to impurities in the feed material. According to patent specifications[65,97], the water content of the starting propene should not exceed 0.001%, that of methylacetylene and allene 0.02%, and the oxygen content should not exceed 0.0005 wt.%†.

c. Organometallic Synthesis

The dimerisation of propene by Ziegler's method[9] in the presence of aluminium alkyl catalysts leads to the formation of pure 2-methylpent-1-ene. Due to the absence of isomerisation reactions, 2-methylpent-1-ene is obtained in up to 95% yield[27]:

$$\overset{\delta^+\ \delta^-}{al{-}CH_2CH_2CH_3} + \overset{\delta^-}{CH_2}{=}\overset{\delta^+}{CH}{-}CH_3 \longrightarrow al{-}CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

$$al{-}CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3 \longrightarrow al{-}H + CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2CH_2CH_3$$

$$\overset{\delta^+\ \delta^-}{al{-}H} + \overset{\delta^-}{CH_2}{=}\overset{\delta^+}{CH}{-}CH_3 \longrightarrow al{-}CH_2CH_2CH_3 \text{ etc.}$$

$(al = \frac{1}{3}Al)$

In addition to the main reaction, "anomalous" addition of propene occurs to a minor extent, giving 5–6% of n-hexenes. The selectivity for dimerisation is strongly dependent on temperature[10,11], pressure, and contact time[10]. Studies of the dimerisation kinetics[100,101] have shown that the reaction order with respect to propene is close to unity. Activation energies of 11.7[100] and 14 kcal $mole^{-1}$ [101] have been reported.

Many modifications of the Ziegler method are known. For example, additions of boron alkyls have been made to the catalyst[102] in order to increase the rate of dimerisation. For the same purpose, various metal additions have been suggested, in particular aluminium, copper, or silver[103], and also salts such as iron(III) chloride[104]. To increase the yield of the propene dimer, the reaction has

† It has recently been announced[139] that the British Petroleum Company has established the production of 4-methylpent-1-ene on a semi-industrial scale (output 2000 tonnes per annum). The bulk of this product is delivered to I.C.I. for the production of polymers. Among the possible uses of 4-methylpent-1-ene we note the dimerisation to 2-isobutyl-6-methylhept-1-ene (in the presence of aluminium alkyls), oxidation to isobutyl methyl ketone in the presence of palladium chloride, autoxidation to epoxyalcohols, isomerisation to 2-methylpent-2-ene, and halogenation[139].

been carried out in a high-boiling organic solvent[105], and the linear velocity of the reactant stream through the reactor has been controlled[106]. Aluminium alkyls containing nickel or platinum compounds[107,108] have also been used as catalysts. An interesting method of dimerisation of alkenes with an internal double bond uses an alkylaluminium containing 1–20 wt. % of alumina–silica, zeolite, silica gel, activated alumina, or other cocatalyst[109].

The Ziegler dimerisation of propene is used as the first stage in the production of isoprene from propene[10,11]. The Goodyear Company, which produces 2-methylpent-1-ene on an industrial scale, has carried out research on the use of the propene dimer as a starting material in industrial organic synthesis[110]. In the Soviet Union, work in this direction is proceeding at the Yaroslavl' Technological Institute[111].

d. Coordination Dimerisation

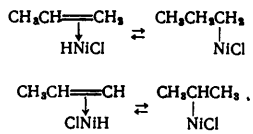
In this Section we shall discuss the dimerisation of propene under the influence of complex organometallic catalysts. The special feature of the mechanism of action of these catalysts is the formation of intermediates consisting of mixed transition metal complexes with alkene ligands. Thus, it is convenient to refer to this type of dimerisation as coordination dimerisation.

The complex catalysts of the Ziegler type, based on alkylaluminium halides and nickel compounds, are extremely active towards the dimerisation of propene under quite mild reaction conditions, and in this respect they are distinctly superior to the catalysts of the types discussed above. For example, a catalyst prepared by mixing 1 mmole of nickel acetylacetonate, 45 mmole of ethylaluminium sesquichloride, and 16 mmole of triphenylphosphine gives 2.6×10^5 moles of the propene dimer (90% yield) in 2 h at 60°C and 10 atm in a toluene medium[19]. The dimer contains 4-methylpent-2-ene (37.0%), 2-methylpent-2-ene (26.5%), 2-methylpent-1-ene (17.4%), 4-methylpent-1-ene (1.6%), 2,3-dimethylbut-1-ene (6%), 2,3-dimethylbut-2-ene (0.5%), hex-2-ene (5.6%), and hex-3-ene (5.6%).[19] A propene dimer containing 75% of methylpentenes and 20% of n-hexenes is formed in the presence of a catalytic system based on π-allylnickel iodide, aluminium bromide, and triphenylphosphine[25]. Replacing the triphenylphosphine by tricyclohexylphosphine yields a dimer containing 67% of dimethylbutenes and 31% of methylpentenes[25]. Catalysts based on π-allylnickel chloride are reported to be used for the dimerisation of propene on a laboratory scale at the Max Planck Institute (Mülheim, W.Germany).[20,112] Trialkylphosphines are added to the catalyst to increase its activity and to obtain products of desired structure[20]. At 30–50°C and 15 atm pressure the conversion of propene is 95%, and the selectivity with respect to the dimer is 88%. The Lurgi–Ruhrgas company has planned an industrial plant for the dimerisation of propene having a capacity of 80 000 tonnes per annum[112]. Its main product is expected to be 2,3-dimethylbut-2-ene, which is intended to be used for the production of 2,3-dimethylbuta-1,3-diene and motor fuel constituents[112]. Dimerisation of ethylene can be achieved in the presence of bis(cyclopentadienyl)nickel[113], and dimerisation of propene by using phosphine complexes of nickel in conjunction with Lewis acids[114].

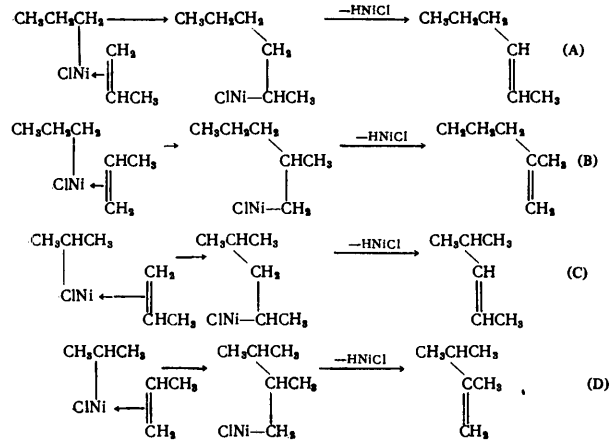
It has been suggested that the activity of complex Ziegler catalysts towards the dimerisation of alkenes[23] and similar reactions[115] arises from the formation of complex hydrides and alkyl derivatives of the transition metal, for example, HNiCl, coordinated to the alkylaluminium halide. The initiation of the dimerisation and the regeneration of the catalyst after each reaction cycle can thus be explained[115]:

$$C_3H_6 + HNiCl \rightarrow C_3H_6NiCl$$
$$C_3H_6NiCl + C_3H_6 \rightarrow C_6H_{12}NiCl$$
$$C_6H_{12}NiCl \rightarrow C_6H_{12} + HNiCl \text{ etc.}$$

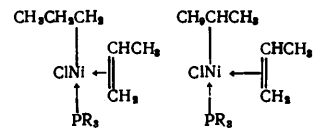
A later, more detailed mechanism for the dimerisation accounts for the structure of the propene dimer and for the influence of tertiary phosphines on the course of the reaction[116]. Two configurations of the alkene ligands are possible in the intermediate π-complexes, leading to the formation of different alkyl derivatives of the transition metal:



The subsequent coordination of a second molecule of alkene can give four types of π-complexes, leading to dimers of different structure:



Paths (B) and (D) are least likely, because of steric hindrance to the formation of the starting π-complexes. But these can be stabilised by the addition of trialkylphosphines to the system[117]:

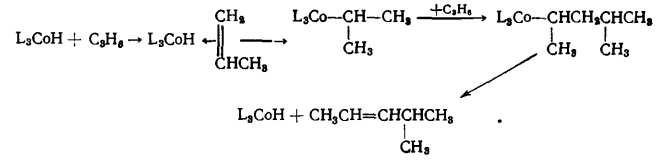


leading to the formation of 2-methylpent-1-ene and 2,3-dimethylbut-1-ene as the primary dimerisation products, which then isomerise to 2-methylpent-2-ene and 2,3-dimethylbut-2-ene respectively.

Complex catalysts based on alkylaluminium halides and nickel salts are active in the isomerisation of alkenes, which occurs under the conditions of the dimerisation reaction and determines the final composition of the reaction products[22,118]. Impurities in the starting alkene can drastically affect the rate of dimerisation of propene[24].

The dimerisation of propene under the influence of cobalt oxide deposited on active carbon can also be classified as coordination dimerisation, because the mechanism proposed by Schultz and coworkers[6] for this reaction includes the formation on the catalyst surface of π-complexes and complex alkyl derivatives of cobalt. This catalyst is peculiar in that large amounts (50–55%) of n-hexenes are formed in its presence. The catalyst is thermally unstable, and

therefore the yield of dimer decreases on raising the temperature (the conversion is 72.7% at the optimum temperature of 85°C). Diene hydrocarbon impurities poison the catalyst irreversibly. The authors suggest that the entity responsible for catalysis is a complex hydride of cobalt having at least one coordination position free to form a π-complex with the alkene[6]:



5. DIMERISATION OF BUTENES AND HIGHER ALKENES

Most of the dimerisation catalysts for ethylene and propene should be suitable, in principle, for the dimerisation of C_4 and higher alkenes. However, practically all the published data relate exclusively to acidic catalysts and organoaluminium compounds, because they offer acceptable yields of the dimers.

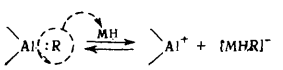
The preparation of the dimer of isobutene in the presence of acidic catalysts (aimed at producing motor fuel constituents) has been known for a long time and does not require special discussion. Higher asymmetrical dialkylethylenes, and also trialkylethylenes, undergo dimerisation similarly to isobutene. For example, 2-methylpent-1-ene in the presence of 70% H_2SO_4 at 50°C dimerises in 30 min with a yield of 80% (on the basis of the added monomer) and 95% (on the basis of the reacted monomer)[111]. High selectivity for the dimerisation of 2-methylpent-1-ene and 2-methylpent-2-ene has been reported for H_3PO_4 on kieselguhr[111] and on an alumina–silica catalyst[119]. It has been pointed out that the dimer of isohexenes boils over a very narrow range of temperatures[111]. The structure of the dimer has recently been investigated[120], and shown to include the following main components: 2,4,4-trimethyl-3-ethylhept-1-ene, 4,6,6-trimethylnon-3-ene, and 4,6,6-trimethylnon-4-ene. Polyanskii and coworkers[121] have investigated the dimerisation of isopentenes on a cation-exchange resin.

In the presence of aluminium alkyls, but-1-ene smoothly dimerises to 2-ethylhex-1-ene, and hex-1-ene to 2-butyloct-1-ene.[9] The dimerisation of butenes by this method has been studied at the Scientific Research Institute of Synthetic Alcohols and Organic Products[122,123].

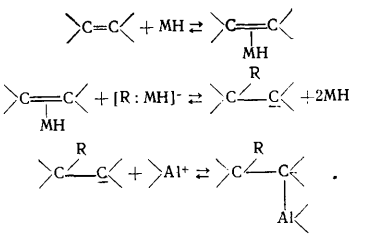
Sladkov and coworkers demonstrated that but-1-ene, but-2-ene, and their mixtures can be used to prepare 2-ethylhex-1-ene in the presence of triethylaluminium and cocatalysts[122]. They proposed a reaction mechanism which explains the role of the transition metal cocatalysts. It is assumed[123] that the interaction between triethylaluminium and the metal compounds (silver, cobalt, nickel, etc.) gives rise to "subcompounds" of the metals in a reduced state according to the scheme

$$M^{+n} \xrightarrow{+me} M^{+(n-m)}.$$

These exist as hydrides or halides (M^+H^- or M^+Cl^- respectively), which are highly electrophilic. The role of the subcompounds in substitution, isomerisation, and polymerisation reactions is discussed. Thus, polymerisation reactions are assisted by "sub-ions" through the formation of active ions from aluminium alkyls:



and they also interact with the double bond and enhance its electrophilic properties:



Alkenes with internal double bonds also dimerise in the presence of aluminium alkyls, but more slowly, and they undergo preliminary isomerisation to the corresponding α-alkenes. Thus, hept-1-ene and hept-3-ene form the same dimer[124]. Dimerisation of alkenes with 3–12 carbon atoms has been proposed[125] in the presence of aluminium alkyls containing trialkylboranes at 195–200°C. For example, hex-2-ene is converted into 2-butyloct-1-ene (in 20% yield) in 4 h under the influence of tri-isobutylaluminium and tributylboron. Similarly, 4-methylpent-1-ene and 2-methylpent-1-ene dimerise to 2-isobutyl-6-methylhept-1-ene. It is thought that trialkylborane promotes the isomerisation of the β-alkene to an α-alkene, which subsequently dimerises[125].

But-1-ene and but-2-ene dimerise at 20°C under the influence of the di-isobutylaluminium chloride–nickel oleate catalytic system (yield of dimer ~ 70%). Infrared and NMR spectral studies of the dimer have shown the presence of 3-methylheptenes, 3,4-dimethylhexenes, and n-octenes, with various positions of the double bond[126].

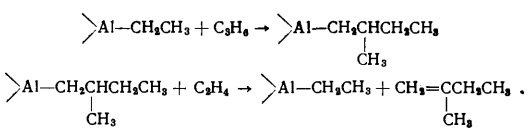
The dimerisation of butenes and hexenes over a cobalt oxide catalyst (13%) supported on carbon has been studied in detail by Schultz and coworkers[6]. After 6 h at 150°C, but-1-ene is converted (13.6% conversion) into a dimer containing 65.3% of n-octenes, 34.4% of 3-methylheptenes, and 0.3% of 3,4-dimethylhexenes. Hex-1-ene gives, after 12 h at 150°C, 18.6% of a product which after hydrogenation contains 82.8% of n-dodecane, 14.8% of 5-methylundecane, and 2.4% of 4-ethyldecane[6]. Alkenes with more than six carbon atoms are dimerised in the liquid phase at 30–40°C over alumina promoted by HF (1%) with 10–20 min contact times. The dimers are used in the production of lubricants and alcohols for the synthesis of plasticisers[127]. Dodecenes have been prepared by the dimerisation of the dimer of propene in the presence of the hydrate of boron trifluoride[128] or of the $BF_3.H_3PO_4$ complex[129].

An interesting method for the dimerisation of higher branched alkenes in the liquid phase relies on brief exposure to high-intensity radiation. The radiation can be in the form of fast electrons, X-rays, gamma rays, or radiation from nuclear reactors[130]. The dimer of di-isobutene was prepared by this method in 74% yield. The mechanism of the radiation-induced dimerisation of higher alkenes has been the object of special investigations[131].

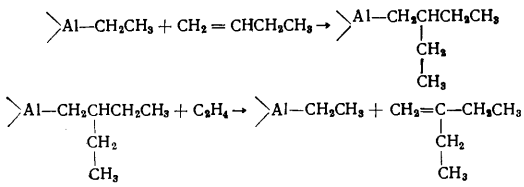
6. CODIMERISATION OF ALKENES

When a mixture of alkenes is used as the starting material, separate dimerisation of each of the alkenes can occur, or alternatively molecules of different alkenes can be combined. In the latter case the term "codimerisation" is appropriate. Most of the catalysts described above allow the codimerisation of ethylene with propene and other alkenes.

The most important application of codimerisation at present is the Ziegler[9] codimerisation of ethylene with propene (or but-1-ene) as a basis for the production of isoprene on an industrial scale[12]. The method depends on the addition of propene to triethylaluminium, followed by the replacement of 2-methylbut-1-ene by ethylene:



Similarly, 2-ethylbut-1-ene can be prepared from ethylene and but-1-ene:



The preparation of isoprene from ethylene and propene has been disclosed in a patent[132]. A mixture of 56.4 g of triethylaluminium and 12.6 g of propene was heated in an autoclave for 30–60 min at 130–140°C. After cooling, a small quantity of "colloidal" nickel was added (as a cocatalyst for the displacement step), 6.72 litres of ethylene were added, and the displacement reaction was carried out by heating the reaction mixture at 160–170°C for 2–3 h. A 20 g yield of 2-methylbut-1-ene was obtained, and subsequently dehydrogenated to isoprene at 700°C on a Fe_2O_3–MgO catalyst, using a 1 : 10 dilution of the vapour. According to another patent[133], 2-methylbut-1-ene can be obtained in ~ 90% yield by the codimerisation of ethylene and propene in a single stage, in the presence of tri-isopentylaluminium at 125–135°C, and with a 3 : 3 : 1 molar ratio of ethylene : propene : $(iso\text{-}C_5H_{11})_3Al$. An interesting method[134] for the simultaneous preparation of 2-methylbut-1-ene and 2-methylpent-1-ene relies on contacting an ethylene–propene mixture with triethylaluminium for 5–50 s at 220–300°C.

Garmonov and Chevychalova[135] prefer to carry out the addition of propene to triethylaluminium at 120–180°C and 40–50 atm, and the displacement reaction at 20°C and 15 atm in the presence of nickel (0.2% on the basis of the aluminium alkyl). Babaev[136] examined some special features of the codimerisation of alkenes in the presence of tri-isobutylaluminium. He attempted to codimerise ethylene with propene in a single stage, but the yield of isopentene did not exceed 30%. In the codimerisation of ethylene with but-1-ene at 225°C, a C_6 fraction containing up to 90% of 2-ethylbut-1-ene is formed in 30% yield[136]. It should be noted that 2-ethylbut-1-ene can be used for the preparation of isoprene by isomerisation to 3-methylpent-2-ene followed by pyrolysis[10].

Normal pentenes are the main product of the codimerisation of ethylene and propene in the presence of alkali metals on carriers[79,91,137]. For example, when potassium supported on talc is used as a catalyst at 115°C, the product obtained from ethylene and propene contains 70% of pent-1-ene, 26% of pent-2-ene, and 4% of hexenes[137]. Ethylene and isobutene undergo codimerisation on a Na/K_2CO_3 catalyst to give a mixture of 2-methylpent-1-ene and 2-methylpent-2-ene in various proportions. The codimer obtained from ethylene and but-1-ene under similar conditions contains 52% of 3-methylpent-1-ene, 21% of 3-methylpent-2-ene, and 27% of n-hexenes. Ethylene and but-2-ene give a product of the following composition: 3-methylpent-1-ene (47%), 3-methylpent-2-ene (16%), hex-2-ene (32%), and hex-3-ene (5%).[79] The product of the codimerisation of ethylene and but-2-ene has been suggested as a starting material for the production of isoprene[138].

Under the influence of complex organometallic catalysts, the alkenes undergo individual reactions as well as codimerisation[22]. When a mixture (1 : 1) of ethylene and propene is passed through a catalyst solution of di-isobutylaluminium chloride and nickel oleate (Al : Ni = 100) at 25°C and 1 atm pressure, the product contains 23% of butenes, 43% of pentenes, 22% of hexenes, and 12% of higher hydrocarbons. The pentene fraction contains 60.7% of pent-2-ene, 35.3% of 2-methylbut-2-ene, 2.6% of 2-methylbut-1-ene, and 1.4% of pent-1-ene.[22] A similar composition of the product is observed when cobalt oxide on carbon is used as the catalyst[7]. In this instance 40% of pentenes is formed, containing ~ 80% of pent-2-ene.

The codimerisation of ethylene with propene under the influence of rhodium chloride in alcoholic solution at 60°C and 1000 atm pressure for 16 h has been described[51]. The product is a mixture of pentenes and hexenes. Analytical hydrogenation of the C_5 alkenes yielded approximately equal amounts of n-pentane and 2-methylbutane.

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Nuclear Magnetic Resonance in Radicals and in Radical Reactions

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The present review examines papers devoted to the application of NMR to the study of the electronic structure of radicals, their solvation by various solvents, and the kinetics of radical reactions. The characteristic features and experimental difficulties of the NMR of radicals in the solid and liquid phases are examined as are the possibility of obtaining data on the mechanism of the delocalisation of the unpaired electron over large distances in the radicals themselves and in their complexes with solvents. It is shown how relaxation methods involving measurement of T_1 and T_2 and the dynamic polarisation of the nuclei have given information on the correlation times characterising the intensity of molecular motions in a liquid, and the energetics of these motions. The theoretical basis of these methods is examined. The last section gives the theory of the use of NMR spectra to measure the rates of various fast reactions. The results of the study of the kinetics of electron transfer and radical substitutions taking place with zero activation energy are discussed. The bibliography contains 61 references.

CONTENTS

Introduction
I. NMR and delocalisation of the unpaired electron in radicals 798
1. NMR of radicals in the solid phase 799
2. NMR of radicals in liquids 800
II. NMR and the solvation of radicals 803
1. Paramagnetic shifts of the solvent nuclei in the presence of radicals 803
2. Single-frequency relaxation methods of studying the solvation of radicals 804
3. Dynamic polarisation of nuclei (two-frequency methods) 806
III. NMR and the kinetics of radical reactions 808

INTRODUCTION

The application of nuclear magnetic resonance to the study of radicals and radical reactions is a new and interesting example of the physical approach to the solution of chemical problems concerning the electronic structure of radicals, their reactivities, and their specific interactions with various molecules. These three aspects make up the contents of the present review. Chief attention is paid to the physicochemical aspects of the phenomena; purely physical aspects which are not of significant importance for chemistry are examined only briefly or not at all.

NMR in radicals gives detailed information on the properties of the molecular orbitals of the unpaired electron and on the mechanism of its delocalisation. The NMR method can give unique data on weak donor–acceptor interactions between radicals and surrounding molecules, on the dynamics of complex-formation equilibria, and on the participation of the unpaired electron in donor–acceptor interactions and the mechanism of its delocalisation in the complex.

Of greatest interest is the possibility of using the NMR method to measure the rates of fast reactions of electron transfer and also radical substitutions, taking place with zero activation energy. This range of problems will subsequently be examined in more detail. We shall restrict ourselves to organic radicals; paramagnetic ions and their complexes with organic ligands will not be considered.

I. NMR AND DELOCALISATION OF THE UNPAIRED ELECTRON IN RADICALS

The molecular orbital of the unpaired electron in radicals usually includes various atomic orbitals of many atoms in the radical. If the nuclei exhibit magnetic moments, the energy of the magnetic electron-nuclear or hyperfine interaction (HFI), measured by the method of electron paramagnetic resonance (EPR), in principle makes it possible to determine the magnitude of the spin density ρ_i. For angle-dependent atomic orbitals (p, d, etc.), ρ_i is determined from the dipole–dipole HFI, and for atomic s orbitals, ρ_i is determined from the isotropic or contact HFI.

A very important characteristic of the behaviour of an unpaired electron, in addition to the magnitude of ρ_i, is the sign of ρ_i, which determines the orientation of the electron spin in the atomic orbital with respect to the orientation of the total spin: $\rho_i > 0$ if these orientations coincide, and $\rho_i < 0$ if they are opposed. The EPR method at best can give only the relative signs of ρ_i (in the study of the EPR of radicals in diamagnetically dilute single crystals[1], or in solutions[2]). The sign of the HFI constants characterises the mechanism of the delocalisation of the unpaired electron over the radical or the mechanism of the "population" of the atomic orbitals—a very important manifestation of electron–electron interactions in the radical.

Let us now consider NMR in a radical. Let us assume that the unpaired electron is situated at an atom with nuclear spin I; the energy levels of the nucleus in a constant magnetic field H_0 with allowance for only the isotropic HFI are then given by the expression

$$E_l = -\gamma_n H_0 m_l + a_l \gamma_e m_s m_l , \qquad (1)$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, m_s and m_i the quantum numbers of the projections of the electron and nuclear spins on the field direction (m_i takes values from $-I$ to $+I$), a_i the constant of the isotropic HFI

$$a_l = \frac{8\pi}{3}\gamma_e\gamma_n|\psi(0)|^2 \qquad (2)$$

and $|\psi(0)|_i^2$ the density of the unpaired electron at a point of the nucleus. The first term in Eqn. (1) corresponds to the Zeeman energy of the nucleus, and the last to the energy of the isotropic HFI.

The magnitude of the local field created by the unpaired electron at a point of the nucleus is $a_i/2(\gamma_e/\gamma_n)$ and for free radicals usually amounts to 10^3–10^4 Oe. This HFI is now not a perturbation of the nuclear Zeeman levels and it displaces considerably the frequency of the nuclear-resonance absorption, so that it becomes non-observable. If, however, the correlation time, that is, the duration of existence of the local field due to the HFI, becomes much shorter than the period of the Larmor precession of the nucleus in this field, this leads to a decrease in the mean value of the local field. In this instance the second term in Eqn. (1) has the form $a_i\gamma_e\langle m_S\rangle m_i$, where $\langle m_S\rangle$ is the mean value of m_S. The value of $\langle m_S\rangle$ is determined by the populations of the electron-spin states $m_S = \pm\frac{1}{2}$. In the high-temperature approximation, when the Zeeman energies are much less than kT, we have

$$\langle m_s\rangle = \sum_{m_s} N_{m_s}m_s \Big/ \sum_{m_s} N_{m_s} \simeq -\frac{\gamma_e H_0}{4kT} \qquad (3)$$

where N_{mS} represents the populations of the states m_S.

For the energy of the transitions $\Delta m_S = 0$, $\Delta m_i = \pm 1$, corresponding to the NMR spectrum we obtain the expression

$$\Delta E = \gamma_n H_0 - a_i\gamma_e(\gamma_e H_0/4kT), \qquad (4)$$

or, converting to the magnitude of the magnetic field at resonance

$$H = H_0 - a_i(\gamma_e/\gamma_n)(\gamma_e H_0/4kT),$$

where H_0 is the resonance field in the absence of HFI. The difference $\Delta H = H - H_0$ is the magnitude of the paramagnetic shift

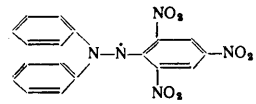
$$\Delta H = -a_i(\gamma_e/\gamma_n)(\gamma_e H_0/4kT). \qquad (5)$$

Thus the fluctuating magnetic field created by the unpaired electron at a point of the nucleus brings about a displacement of the resonance frequency of this nucleus, whose magnitude and sign are determined by the magnitude and absolute sign of the constant a_i. It is necessary only that the frequency of the fluctuations in the local field be much greater than the frequency of the Larmor nuclear precession in this field. It is evident that the paramagnetic shift of the NMR in radicals is analogous to the Knight shift of the NMR in metals, due to the contact HFI of the nuclei with the conductivity electrons[3].

The condition for observability of the paramagnetic shift is that the duration τ of the existence of the local field of the HFI should be short compared with the period of the nuclear precession in this field, that is, $\tau \ll a_i^{-1}$, where a_i is expressed in frequency units. Since the spin-lattice relaxation time T_1 in radicals is usually large, this mechanism cannot ensure that the condition $T_1 \ll a_i^{-1}$ is satisfied; the most important part is taken by the mechanism of the electron–electron exchange interactions taking place in concentrated solid or liquid solutions of the radicals. This corresponds to the mutual reorientation of neighbouring electron spins with exchange frequency ω_{ex}; in crystals of the radicals $\omega_{ex} \simeq 10^{10}$–$10^{11}$ s^{-1}, that is, the electron changes its orientation 10^3–10^4 times within the period of the nuclear precession. This is sufficient to average the local fields created by the HFI, except for the small residual fraction obeying the Boltzmann distribution; it is this HFI which is responsible for the paramagnetic shift.

1. NMR of Radicals in the Solid Phase

NMR in diphenylpicrylhydrazyl (DPPH)



has been studied in most detail.

From the structure of the radical it follows that there are four groups of equivalent protons, and in the NMR spectrum these should correspond to four lines with integral intensities in the ratio 1 : 2 : 2 : 1, proportional to the number of protons of each kind. In the first experiments, however, only two strongly overlapping lines were observed[4] and only later was it possible to resolve the spectrum completely[5]. The NMR spectrum of polycrystalline DPPH, taken in the form of the 1 : 1 complex with benzene, is shown in Fig. 1*a*. It can be seen that in addition to the four expected lines there appears in the centre an additional line which is not displaced and which corresponds to complexed benzene. If benzene is replaced by deuteriobenzene, the intensity of this line decreases sharply; there remains only a small peak which apparently corresponds to diamagnetic impurities in the radical (Fig. 1*b*). Replacement of the *meta*-protons in the picryl group by deuterium showed that the resonance of these protons is displaced considerably to low fields (Fig. 1*c*).

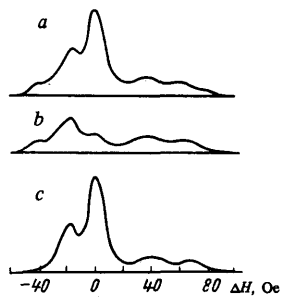


Figure 1. NMR spectra of polycrystalline DPPH at 4.2°K. *a*) DPPH in its 1 : 1 complex with benzene; *b*) DPPH in its complex with deuteriobenzene; *c*) DPPH with deuterium in the picryl group.

On the basis of these data, and also from calculations of the spin densities by the valency bond method, and from the intensities in the spectrum, it was assumed that the resonance of the *meta*-protons is displaced to low fields, and that the resonance of the *ortho*- and *para*-protons is displaced to high fields; the paramagnetic shifts and HFI constants a_H, calculated from Eqn. (5), are given in Table 1.

In view of the approximate nature of the theory and the experimental errors, the agreement is fairly good. Thus at the hydrogen atoms in the *ortho*- and *para*-positions of the phenyl rings, the spin density is negative, whereas it is positive in the *meta*-positions. These conclusions were confirmed in later work; it was shown that the

dependence of the paramagnetic shift on the magnetic field intensity and on temperature obeys Eqn. (5) satisfactorily[6].

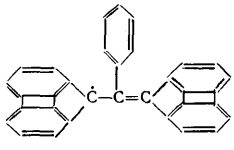
In DPPH, as in most other aromatic radicals, the unpaired electron is a π-electron and its molecular orbital is made up from the orbitals of the nitrogen atoms and the π-orbitals of the carbon atoms of the aromatic system. The isotropic HFI at the protons attached to these carbon atoms appears as a result of $\sigma-\pi$ configurational interaction, that is, partial unpairing of the electrons of the C–H bond; the signs of the spin density at the carbon atom and the hydrogen atom attached to it are opposite. This means that in DPPH there is positive spin density at the carbon atoms in the *para*- and *ortho*-positions, and negative spin density at the carbon atoms in the *meta*-positions. Thus the unpaired electron in DPPH is delocalised over the π-system of the radical; its density ρ at the carbon atoms in the rings can be determined from the familiar McConnell relationship[7] $a_H = Q\rho$, where $Q = 23.7$ Oe,[8] and the constants of the isotropic HFI at the neighbouring protons are determined either from the EPR spectra (without signs), or from NMR data, as for DPPH (Table 1).

Table 1. Paramagnetic shifts and HFI constants in DPPH.

Position of protons	ΔH, Oe	a_H, Oe (experiment)	a_H, Oe (theory) (Ref.5)
Picryl (*meta*)	−38	+2.4	+2.55
Phenyl (*meta*)	−16	+2.1	+1.55
Phenyl (*ortho*)	+37	−2.3	−2.94
Phenyl (*para*)	+62	−3.9	−2.74

An interesting feature is that the central line in the NMR spectrum of DPPH, corresponding to the protons of the benzene in the complex with DPPH, is not displaced, that is, the spin density at the atoms of the ligand in the complex is very low, although the complex itself is fairly stable.

The NMR spectrum of 1,3-bis(biphenylene)-2-phenylallyl:



shows some structure even at 77°K. At 4.2°K, two lines are clearly observed; one of these is displaced to high fields by 15 ± 1 Oe, and the other, whose intensity corresponds to ~ 70% of the total intensity of absorption, remains almost unshifted[9].

The EPR spectrum of this radical contains 9 lines with splitting 2.2 Oe. It is not known which protons produce this splitting; nevertheless, it is possible to divide all the protons in the radical into two groups: 8 protons with HFI constant 2.2 Oe, and the other 13 protons with very slight splitting. Since the radical is present in the crystal as the 1 : 1 complex with benzene, the NMR spectrum should contain two lines—one displaced (from the 8 protons) and one which is not displaced (from the 13 + 6 = 19 protons). The observed NMR spectrum shows complete agreement with these ideas. At the protons giving an HFI constant of 2.2 Oe, the spin density is negative (paramagnetic shift to high fields), that is, at the carbon atoms to which these protons are attached, the density of the unpaired π-electron is positive and is much greater than the density of the unpaired electron at the other carbon atoms.

The NMR spectrum of the pyrene radical-anion, in addition to a line which is not displaced and which corresponds to the diamagnetic original substance, contains three displaced lines[10]. The signs and magnitudes of the HFI constants are given in Table 2, which also gives for comparison the values of the same constants obtained by the EPR method; the agreement is very good.

Table 2. Paramagnetic shifts and HFI constants in the pyrene radical-anion.

ΔH, Oe	a_H(NMR)	a_H(EPR)
−35.1	+1.26	(+) 1.09
+79.1	−2.79	(−) 2.08
+140.5	−4.88	(−) 4.75

The NMR spectrum of the tri-*p*-chlorophenylammonium radical-cation at 77°K consists of two poorly resolved lines with equal intensity, one of which is displaced by 2.3 Oe to low fields, whereas the other is displaced by 3.9 Oe to high fields. These lines evidently correspond to the *ortho*- and *meta*-protons, on which the spin densities have positive signs[9].

In addition to the study of these radicals, attempts have also been made to study NMR in the polycrystalline tetramethyl-*p*-phenylenediamine radical-cation (Wurster's cation), but definite results could not be obtained[9]. This is apparently due to the fact that at fairly high temperatures the paramagnetic shifts are small, and at low temperatures the crystal is converted into an antiferromagnetic state[11].

2. NMR of Radicals in Liquids

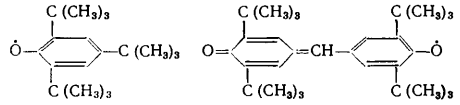
Until now we have examined the paramagnetic shift due only to the isotropic HFI. The anisotropic part of the HFI also produces a shift, whose magnitude and sign are determined by the magnitude and sign of the anisotropic HFI constant; the latter can be found from the paramagnetic shifts in single crystals of radicals. In polycrystalline specimens, the anisotropic HFI leads to marked broadening of the lines; it is for this reason that paramagnetic shifts in polycrystalline specimens can be observed only at very low temperatures, when the magnitude of the shift is greater than the width of the lines. In liquids, the anisotropic HFI is averaged by the molecular motion, and the NMR lines become much narrower.

The condition for observation of the paramagnetic shift is satisfied only in concentrated solutions of radicals. The width of the lines is determined by both the dipole and scalar relaxations (see Section II) and is usually proportional to a^2; the condition for obtaining very narrow lines $\omega_S^2 \tau_{ex}^2 \ll 1$ is difficult to satisfy for solutions of radicals,

in contrast to the situation for paramagnetic ions, where the electronic relaxation times T_{1e} are often small and $\omega_S^2 T_{1e}^2 < 1$.

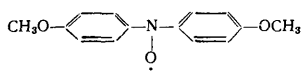
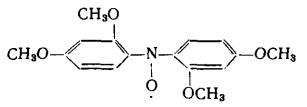
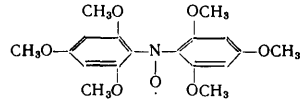
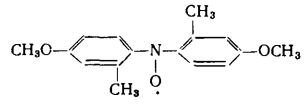
Most studies have naturally been carried out with stable radicals. This, however, does not restrict the possibilities of using the method for the main task—the investigation of the mechanism of delocalisation of electrons in many-electron molecular systems.

In the NMR spectra of 2,4,6-tris-t-butylphenoxyl and Coppinger's radical:



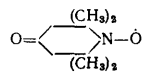
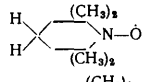
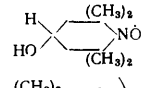
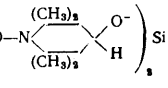
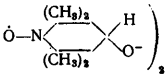
recorded at 20° in C_6D_6, the lines of the *o*-t-butyl protons are displaced to low fields relative to the same protons in the corresponding molecules, that is, there is positive spin density at these protons; the HFI constants are +0.071 Oe and +0.049 Oe respectively, and show good agreement with the constants obtained by the EPR method (0.072 Oe and 0.049 Oe)[12]. Calculation of the spin density in these radicals shows that in the *ortho*-positions of the rings there is positive π-electron density, that is, the signs of the spin densities at the carbon atoms in the *ortho*-position and the *o*-t-butyl protons are the same; this apparently means that the chief part in delocalisation of the unpaired electron on the protons of the t-butyl groups is played by the hyperconjugation mechanism (further proof of this is given below, in section II).

Table 3.

Radical	HFI constants for the protons of the CH_3 and OCH_3 groups, Oe	
	para-position	*ortho*-position
	+0.223	—
	+0.180	+0.100
	+0.120	+0.084
	+0.075	+0.160

In aromatic nitroxide radicals (Table 3) the sign of the constant a_H on the protons of the *ortho*- and *para*-substituents also coincides with the sign of the π-electron spin density on the corresponding carbon atoms of the aromatic rings; this means that the unpaired electron appears in the atomic orbitals of the CH_3 and OCH_3 hydrogen atoms due to a hyperconjugation mechanism[13]. The values of a_H for OCH_3 in a series of radicals (Table 3) gradually decrease; this may be due to a decrease in the spin density in the rings as a result of the twisting due to steric interaction of the *ortho*-substituents[14]. The relationship between the constants a_H for OCH_3 in the *ortho*- and *para*-positions, and also between a_H for OCH_3 and CH_3 is the same as that usually observed in EPR for radicals of this type[15]. Extremely interesting characteristic featues of the delocalisation of an unpaired electron in a σ-system are observed in aliphatic nitroxide radicals[16,17]. The HFI constants in some of these radicals are given in Table 4.

Table 4.

No.	Radical	HFI constants for the protons, Oe			
		β-CH_3	β-CH_2	γ-CH	other protons
I		—0.1	0		
II		—0.2	—0.4	+0.15	
III		0 and —0.43	—0.32 and —0.46	+0.08	
IV		0 and —0.43	—0.31 and —0.46	+0.08	~0
V		0 and —0.4	—0.29 and —0.5	+0.09	

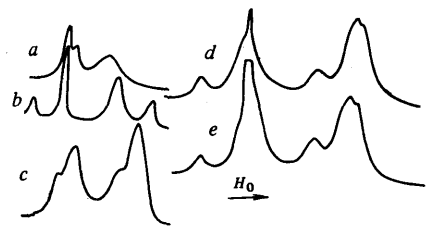


Figure 2. NMR spectra of radicals: I at 50°C (*a*); II at 36°C [16] (*b*); III at 25°C (*c*) and 60°C (*d*); IV at 60°C (*e*). Spectra recorded at 100 mHz (see Table 4).

The NMR spectra of some of these radicals are given in Fig. 2. In radicals I and II the protons of all the β-CH_3 groups are equivalent and give a single line in the NMR spectrum; the protons of the β-CH_2 groups are also equivalent. In the radicals and polyradicals III–V, the NMR signal of the protons of the β-CH_3 groups consists of two lines which are displaced considerably relative to one another. The HFI constants for these radicals differ considerably from one another for both the β-CH_3 groups and the β-CH_2 groups. This means that these groups are nonequivalent: for two of them, the constants a_H are close to

zero, and for the other two the values lie between −0.38 Oe and −0.42 Oe. The mean value of these constants corresponds exactly to the HFI constant for the β-CH_3 protons in radical II. The spatial configurations of the aliphatic rings in radicals III–V are evidently fixed, and the frequencies of the inversion transitions (of the "chair"–"boat", "chair"–"chair" type etc.) are small compared with the difference in the HFI constants of the protons of the non-equivalent β-CH_3 groups. In radical II the frequencies of these inversions are high so that the averaged HFI constant for all the β-CH_3 protons is observed.

A similar picture is observed for the protons of the β-CH_2 groups; here also they are non-equivalent in radicals III–V, but in radical II they are equivalent with a mean value for the HFI constant equal to half the sum of the HFI constants of the non-equivalent protons of the β-CH_2 groups.

These results show that the unpaired electron is delocalised over the angular orbitals, that is, by a hyperconjugation mechanism (at least on the β-carbon atoms). The presence of a π-electron on the C atom in CH_3 was also proved by the EPR method[18]; it was found that the sign of the constant $a_{^{13}C}$ for CH_3 coincides with the sign of the π-electron spin density $\rho^{\pi}_{^{13}C}$ for the same ^{13}C atom. If it is assumed that the signs of a_H and $\rho^{\pi}_{^{13}C}$ coincide (this assumption is justified by EPR spectroscopy), it follows that there is negative π-electron spin density on the β-carbon atoms. It should be noted that at the N atom the spin density is positive and large: $\rho^{\pi}_N \simeq 0.8$.[19] It is at present difficult to resolve unambiguously the problem of the mechanism of the appearance of negative spin density on β-CH_3 and β-CH_2. It is also not clear why $a_H > 0$ at the protons of the γ-CH group, in contrast to the situation for all other protons of the aliphatic ring. One reasonable explanation can be found in the assumption that there is direct spatial overlap of the γ-CH sp^3 hybrid orbitals and the π-orbital of the nitrogen atom; evidence for this is provided by the fact that a_H for γ-CH in radicals III–V is smaller by a factor of almost two than a_H for γ-CH_2 in radical II.

Recently, considerable attention has been paid to the use of the NMR method to study paramagnetic solutions of aromatic hydrocarbons in the presence of alkali metals. The radical-anions formed take part in fast electron exchange with neutral molecules of the aromatic hydrocarbons; the characteristic time of this reaction is the correlation time of the averaged isotropic HFI. The observed paramagnetic shift is similar in character to that in the examples examined above, and the magnitude of the shift is given by Eqn. (5), in the right-hand side of which appears a new factor f_M—the mole fraction of the ion-radicals (see section III for more details).

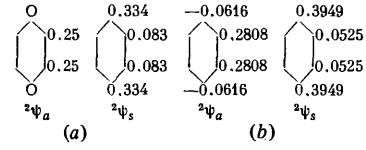
The signs and magnitudes of the isotropic HFI constants on the protons of the alkyl groups in the radical-anions of 1- and 2-alkyl substituted naphthalenes have been determined[20] (Table 5). For the α-protons, the signs of the HFI constants were determined from the NMR spectra, and their absolute values were found from the EPR spectra.

The NMR spectra of the p-xylene and p-diethylbenzene radical-anions[21,22] showed that the spin density on the α-protons of the alkyl groups is negative ($a_{CH_3} = -0.083$ Oe in the p-xylene anion and $a_{CH_2} = -0.050$ Oe in the p-diethylbenzene anion). Calculations show that the isotropic HFI for these protons appears as a result of hyperconjugation. (This can also be seen from the experimental data: the value of a for CH_2 in the p-diethylbenzene anion is less than that for CH_3 in the p-xylene anion—this situation is characteristic of the delocalisation of an electron over the angular orbitals.) This means that the sign of the spin density for CH_3 and CH_2 in these anions is the same as that of the spin density on the carbon atoms to which these groups are attached. This raises the problem of how the negative spin density appears on these carbon atoms.

Table 5. HFI constants at the α-, β-, and γ-protons of the substituents in naphthalene radical-anions.

Substituent	HFI constants × 10^3, Oe				Substituent	HFI constants × 10^3, Oe			
	α	β	γ	δ		α	β	γ	δ
1-CH_3	+3860				2-CH_3	+1810			
1-C_2H_5	+3240	− 74			2-C_2H_5	+1130	+32		
1-n-C_3H_7	+2670	−212	+64		2-n-C_3H_7	+1080	−2	+27	
1-n-C_4H_9	+2800	−155	+45	+35	2-n-C_4H_9	+1050	—	—	+20

The xylene anion can be regarded as a weakly perturbed benzene system. The degeneracy of the ground state of the benzene anion is removed by the perturbing influence of the two CH_3 groups but the splitting between the levels remains very small. EPR studies show that in 1- and 1,4-substituted benzene anions the lowest antibonding orbital is antisymmetric with respect to reflection in a plane perpendicular to the plane of the molecule and passing through the two CH_3 groups. The other orbital, which is symmetric, should have a slightly higher energy. The distribution of the spin density for each of these two orbitals is shown in the scheme below:



Since the unpaired electron occupies the lowest antisymmetric orbital $^2\psi_a$, its density at carbon atoms 1 and 4 should be equal to zero, so that the HFI splitting for the CH_3 protons should also be equal to zero. Since this splitting is not equal to zero, however, Bolton and coworkers[23] proposed three possible mechanisms which might lead to the observed effect: (a) vibronic or electronic-vibrational interactions between the symmetric and antisymmetric states; (b) thermal excitation, which with increase in temperature increases the spin population of the symmetric state; and (c) configuration interaction between the ground and excited states $^2\psi_a$ and $^2\psi_s$; mechanisms (a) and (b) should make a positive contribution to the HFI constant. Thus mechanism (c) apparently determines the sign of the HFI constant.

For a quantitative estimate of all these contributions, it is necessary to examine the results of the calculation of the spin density at all the carbon atoms in the $^2\psi_a$ and $^2\psi_s$ states[24]. These results [with allowance for the configurational interaction according to mechanism (c) and the inductive influence of the CH_3 groups] are given in scheme (b). If it is assumed that the splitting for the CH_3 in the p-xylene anion is proportional to ρ_1 (or ρ_4) with proportionality constant +25 Oe, the magnitude of this splitting should amount to −1.50 Oe. Experiment gives only −0.1 Oe, that is, the sum of the positive contributions of mechanisms (a) and (b) compensates almost completely

the contribution of mechanism (c). Thus the splitting for CH_3 is almost independent of temperature, if it is assumed that the contribution of mechanism (b) is very small and that the chief part is played by the competing mechanisms (a) and (c).

In the mono-substituted radical-anions of toluene, ethylbenzene, and cumene, the spin density on the α-protons is positive and depends markedly on temperature; this is indicated both by the NMR spectra of the anions and by EPR studies of these anions[22]. Here, the main contribution to the splitting is apparently made by mechanism (b); from the temperature dependence of the splitting at CH_3 in the toluene anion it was found that the energy gap between the $^2\psi_a$ and $^2\psi_s$ states amounts to 2.8 kcal mole^{-1}.[19]

Although the NMR method makes it possible to measure the absolute values of the HFI constants (at fairly small values of ~ 0.1–0.01 Oe), and also in a number of instances to improve the assignment of these constants made from EPR studies of the radicals, its chief role is nevertheless the determination of the signs of the HFI constants. It is for this reason that the NMR method has played an exceptional role in the development of the theory of isotropic HFI and has made an important contribution to ideas regarding the mechanisms of the delocalisation of the unpaired electron in radicals.

II. NMR AND THE SOLVATION OF RADICALS

In the condensed phase, radicals very often form complexes of the donor–acceptor type with molecules of the surrounding medium. This complex formation alters considerably the reactivity of the radicals[25], so that the study of the nature of the electronic interactions in the complex of the radical with the solvent molecules (for the sake of brevity these will subsequently be described arbitrarily as ligands) is of considerable interest. If the molecular orbital of the unpaired electron in the complex also includes the orbitals of the ligand, that is, if the unpaired electron is delocalised over the ligand, an isotropic HFI, whose magnitude and sign are determined by the mechanism of delocalisation of the electron, appears at the magnetic nuclei of the ligand. This HFI of the solvent nuclei can be detected by the NMR method, from the paramagnetic shifts or from the anomalies in the ratios of the nuclear relaxation times T_1/T_2 (single-frequency methods) or from the magnitude and sign of the dynamic polarisation of the nuclei (two-frequency methods). We shall examine briefly all these methods, and we shall analyse the "chemical" information obtained up to the present by these methods.

1. Paramagnetic Shifts of Solvent Nuclei in the Presence of Radicals

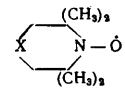
The solvation of paramagnetic species, in particular organic radicals, may be accompanied by delocalisation of the unpaired electron over the molecules of the solvent and the appearance of an isotropic HFI at the nuclei of the solvent. As with radicals, this HFI leads to a paramagnetic shift of the solvent nuclei, whose magnitude and sign are determined by the HFI constants. The only difference from the situation for radicals is in the mechanism of the averaging of the HFI aIS: in radicals, averaging of the spin fraction of the HFI takes place as a result of exchange interaction, but the condition for the observation of paramagnetic shifts of solvents is the modulation of a with a frequency τ_e^{-1} such that $a^2\tau_e^2 \ll 1$; the mechanism of the modulation of a is usually associated with the formation and decomposition of complexes of the radical with solvent molecules. The expression for the paramagnetic shift has the form (its derivation is given in section III):

$$\Delta H = -af(\gamma_e/\gamma_n)(\gamma_e H_0/4kT);$$

$f = nN/N_0$ is the mole fraction of the solvent molecules in the complex with the radicals, N the number of molecules of the radical species, N_0 the number of solvent molecules per unit volume, and n the coordination number of the solvate.

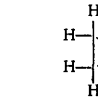
These complexes are essentially ideal models for studying the mechanism of delocalisation of the unpaired electron. Unfortunately, very little work has yet been done on the paramagnetic shifts of solvents in the presence of organic radicals.

Richards and coworkers[26] observed the paramagnetic shift of the fluorine nuclei of C_6F_6 in the presence of tris-t-butylphenoxyl; a_F is positive and amounts to ~ 4 Oe. The paramagnetic shifts of the protons of a series of solvents have been studied in the presence of nitroxide radicals



with **X** = CH_2, CO, or CHOH [27] (Table 6).

Table 6.

Solvent molecule	HFI constant for the protons, Oe			
	OH	α-CH	β-CH	other protons
H_2O	−0.56			
HOD	−0.56			
$\bar{O}H$	−1.27			
CH_3OH	−0.485	+0.066		
CH_3CH_2OH	−0.363	+0.058	+0.025	
$(CH_3)_2CHOH$	−0.363	+0.044	+0.013	
$(CH_3)_3COH$	—		0.01	
$(CH_2OH)_2$	−0.264	+0.074		
$PhCH_2OH$	−0.52	+0.055		
$CH_2{=}CH{-}CH_2OH$	—	+0.033	+0.055	
CH_3COOH	−0.435		0	
$HCCl_3$				−0.396
H_2CCl_2				−0.088
$(CH_3CH_2)_2NH$		+0.033	+0.018	−0.051
		+0.04		−0.3

The HFI appears at the protons in the molecules of those solvents which take part in donor–acceptor interactions (of the hydrogen bonding type) with the radical (Table 6). Analysis of the HFI shows a number of characteristic features of the delocalisation of the unpaired electron in the solvate complex. Firstly, at the protons forming a hydrogen bond with the paramagnetic centre of the radical, the spin density is always negative. Secondly, at the α- and β-protons the HFI constant is positive and its magnitude decreases along the aliphatic chain. Comparison of the HFI constants for the α- and β-protons in a series of alcohols shows that at the α- and β-carbon atoms the unpaired electron is situated in angular orbitals (apparently quasi-π-orbitals) and it appears in such orbitals by a hyperconjugation mechanism. This mechanism

assumes the presence of positive π-electron spin density on the atomic orbitals of the oxygen or nitrogen in alcohols or amines; this possibly results from direct overlap of the π-orbitals of the radical and the atomic orbitals of the O and N atoms in the complex. The negative spin density on the protons taking part in hydrogen bonding then arises by a spin polarisation mechanism (as in the $\gg$CH fragment). An interesting feature is that in $\overline{\text{O}}$H, where direct overlap of the orbital of the unpaired electron with the orbitals of the O atom should be greater than in other instances, the HFI constant at the H atom is also much greater. At the protons of the amino-group, on the other hand, this constant is very small; here the negative spin density, produced by the spin polarisation mechanism, apparently compensates to a considerable extent the contribution of the positive density from the unpaired electron in the NH orbitals, partly hybridised with the electron pair of the nitrogen†.

2. Single-frequency Relaxation Methods for Studying the Solvation of Radicals

The kinetics of the change in nuclear magnetisation in NMR are usually defined by two kinetic constants: the spin-lattice or longitudinal relaxation time T_1, characterising the rate of the approach of the z component of the nuclear magnetisation to the equilibrium corresponding to the Boltzmann population of the nuclear Zeeman levels, and the transverse relaxation time T_2, determining the rate of the approach of the total x and y components of the magnetisation to zero, that is, the approach to dephasing of the nuclei (z is the direction of the external magnetic field). Physically, longitudinal relaxation corresponds to inversion of the nuclear spins (exchange of energy takes place between the spin system and the lattice). The transverse relaxation is related both to the longitudinal relaxation and to the presence of local magnetic fields which alter the frequency of precession of each spin and lead to dephasing of the nuclei; complete dephasing corresponds to zero values of the x and y components of the magnetisation of the complete spin system.

A physical model of nuclear relaxation in a liquid was proposed by Bloembergen and coworkers[28] as early as 1948. It was based on the fact that the disordered molecular motion of the species in a liquid leads to fluctuations of the local fields produced by the dipole–dipole interaction of the nuclei. A contribution to T_1 is made only by the x and y components of the fluctuating field, whereas contributions to T_2 are made not only by these fluctuations but also by the z components of the local field. The usual method for calculating T_1 and T_2 involves the determination of spectroscopic densities, that is, the Fourier transforms of the correlation functions describing the dipole–dipole interaction modulated by the molecular Brownian motion. T_1 contains the spectroscopic densities $J(\omega)$ and $J(2\omega)$, where ω is the Larmor precession frequency of the nuclei, and T_2 also contains $J(0)$, corresponding to the dephasing of the nuclei in the local fields created by the fluctuating z component.

Nuclear relaxation in the presence of paramagnetic species is described in principle in the same way. The dipole–dipole electron–nuclear interaction operator has the form

$$H' = \gamma_e\gamma_n \frac{ISr^2 - 3(Ir)(Sr)}{r^5}.$$

In polar coordinates, this can be represented in the more explicit form

$$H' = \gamma_e\gamma_n(A+B+C+D+E+F),$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, I and S the spin operators of the nucleus and the electron, r the distance between the electron and the nucleus, and the operators A–F have the forms:

$$A = r^{-3}(1-3\cos^2\theta)I_zS_z,$$
$$B = -\frac{1}{4}r^{-3}(1-3\cos^2\theta)(I_+S_- + S_+I_-),$$
$$C = -\frac{3}{2}r^{-3}\sin\theta\cos\theta\, e^{-i\varphi}(I_zS_+ + I_+S_z),$$
$$D = -\frac{3}{2}r^{-3}\sin\theta\cos\theta e^{i\varphi}(I_zS_- + I_-S_z),$$
$$E = -\frac{3}{4}r^{-3}\sin^2\theta e^{-2i\varphi}I_+S_+,$$
$$F = -\frac{3}{4}r^{-3}\sin^2\theta e^{2i\varphi}I_-S_-,$$

where $I_\pm = I_x \pm iI_y$, $S_\pm = S \pm S_x \pm iS_y$, and the spatial parts of the operators are the spherical functions Y_2^0, $Y_2^{\pm1}$, and $Y_2^{\pm2}$. T_1 contains the spectroscopic densities $J(\omega_I - \omega_S)$, $J(\omega_I)$, and $J(\omega_I + \omega_S)$, corresponding to the correlation functions of the operators B, C, and D, and E and F, and T_2 also contains $J(0)$ and $J(\omega_S)$, corresponding to the operators A, C, and D.

Since in liquids with low viscosity the correlation time of the molecular motions τ_C is small (10^{-11}–10^{-12} s), we have $\omega_I^2\tau_C^2 \ll 1$ and $\omega_S^2\tau_C^2 \ll 1$, when all the spectroscopic densities become independent of ω and equal to $J(0)$ and $T_1 \simeq T_2$ (these become equal to the extent to which the inequality $\omega_S^2\tau_C^2 < 1$ is satisfied). This is the case of strong narrowing, when relaxation of the transverse components of the magnetisation takes place only by spin-lattice relaxation. Relaxation in the presence of most paramagnetic ions obeys this theory; equality of T_1 and T_2 is effectively observed.

An anomaly in the ratio T_1/T_2 was first observed for the protons of water in solutions of Mn^{2+} and Gd^{3+} salts, where it was found that $T_1/T_2 > 1$; this phenomenon was subsequently observed in aqueous solutions of a number of other ions.

Bloembergen[29] attributed this anomaly in the ratio T_1/T_2 to the presence of isotropic HFI of the solvent nuclei with the unpaired electron of the paramagnetic species. This interaction may take place in the complex formed by the paramagnetic species with the solvent molecules as a consequence of the finite density of the unpaired electron at the nuclei of the solvent.

The isotropic interaction aIS can be represented by the operator $H'' = aI_zS_z + \frac{1}{2}a(I_+S_- + I_-S_+)$, where the first term, whose spin part corresponds to the spin part of the operator A of the dipole interaction, makes a contribution to $J(0)$ (secular part), and the second term, with spin part similar to the operator B, makes a contribution to $J(\omega_I - \omega_S)$.

For the contribution of the interaction H'' to the relaxation to be significant, it is necessary to have mechanisms leading to time modulation of H''. Two main mechanisms of such modulation can be pictured. Firstly, change in the constant a with correlation time τ_e, which has the significance of the lifetime of the complex formed by the

† The structure of the complexes and the mechanisms of the delocalisation of the unpaired electron in complexes with hydrogen bonding and in π-complexes have been discussed in more detail elsewhere [59].

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solvent molecule with the paramagnetic species; it is assumed that a depends markedly on distance; it is equal to a during the existence of the complex and is equal to zero when the complex decomposes. The relaxation due to this mechanism is called first-order scalar relaxation. Secondly, aIS may be modulated by the longitudinal relaxation of the spin of the electron; the correlation time of the interaction aIS then becomes the electronic relaxation time T_{1e}; this is second-order scalar relaxation. In solutions of organic radicals, T_{1e} is usually large, and the main contribution to the relaxation is made by the modulation of a.[30]

Rigorous examination of both contributions—dipole and isotropic—to the relaxation according to the scheme outlined briefly above gives the following expressions for T_1^{-1} and T_2^{-1} for $\omega_I^2\tau_C^2 \ll 1$:

$$\frac{1}{T_1} = \frac{\gamma_I^2\gamma_S^2\hbar^2 Nn}{10r_0^6 N_0}\left(3\tau_c + \frac{7\tau_c}{1+\omega_S^2\tau_c^2}\right) + \frac{1}{2}\left(\frac{A}{\hbar}\right)^2 \frac{Nn}{N_0}\left(\frac{\tau_e}{1+\omega_S^2\tau_e^2}\right), \quad (6)$$

$$\frac{1}{T_2} = \frac{\gamma_I^2\gamma_S^2\hbar^2 Nn}{20r_0^6 N_0}\left(7\tau_c + \frac{13\tau_c}{1+\omega_S^2\tau_c^2}\right) + \frac{1}{4}\left(\frac{A}{\hbar}\right)^2 \frac{Nn}{N_0}\left(\tau_e + \frac{\tau_e}{1+\omega_S^2\tau_e^2}\right), \quad (7)$$

where τ_C and τ_e are the correlation times of the dipole interaction and the isotropic HFI, N and N_0 the numbers of radical species and solvent molecules in 1 cm³, and n the coordination number of the complex. The first terms in (6) and (7) evidently correspond to the dipole contribution to the relaxation, and the second terms to the contribution of the isotropic HFI. It can also readily be seen that the ratio $T_1/T_2 > 1$ only when the correlation time τ_e is sufficiently large; with this condition, a contribution to T_2 is made by the spectroscopic density $J(0)$ produced by the secular part of the isotropic HFI. In the limit, for $\omega_S^2\tau_e^2 \gg 1$, the second term in T_1^{-1} is equal to zero, and the contribution of this term to T_2^{-1} is $\frac{1}{4}(a/\hbar)^2\frac{Nn}{N_0}\tau_e$.

It is evident that the anomaly in T_1/T_2 is greater, the greater a and τ_e (but τ_e should not be greater than a^{-1}). At small values of τ_e (weak complexes) or in weak fields (ω_S small), we may have $\omega_S^2\tau_e^2 \ll 1$, so that again $T_1/T_2 = 1$; physically, this means that although scalar interaction aIS takes place in the complex, the contribution of the secular terms $J(0)$ in T_2 becomes negligible.

The method involving determination of the ratio T_1/T_2 has found extensive application for the study of the complexes formed by paramagnetic ions with ligands; little work has been done on radicals.

The first paper was published in 1963. Gutowsky and Tai[31] determined T_1 and T_2 for protons in various solvents —chloroform, dioxan, benzene, acetonitrile, water, dichloroethane, tetramethylsilane, and cyclohexane—in the presence of DPPH and the di-t-butylnitroxide radical. T_1^{-1} and T_2^{-1} were linearly dependent on the concentration of radicals, but the ratio T_1/T_2 was found to be constant for all concentrations and equal to 1.1–1.2, that is, its value was very close to unity. For the fluorine nuclei in hexafluorobenzene and 1,3,5-trifluorobenzene, however, T_1/T_2 differed significantly from unity and amounted to 1.40–1.70. These results show that in the complexes formed by fluorine-containing molecules with radicals, the unpaired electron is delocalised over the atomic orbitals of the ligand, the constants of the isotropic HFI at the fluorine nuclei being sufficiently large (10^6–10^7 s^{-1}) to make a secular contribution to T_2. The fact that for the protons $T_1/T_2 \simeq 1$ shows that a_H may be much less than a_F. This makes it very difficult to decide whether the complex has a structure of the π-complex type, or whether there is localised interaction in the complex between the radical and the fluorine atom of the molecule.

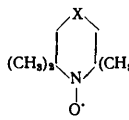
Sagdeev and Molin[32] determined T_1 and T_2 for the protons of biphenyl, naphthalene, nitrobenzene, and nitromethane in the presence of DPPH. They found that the values of T_1/T_2 differ considerably from unity and established a relationship between this deviation and the ionisation potentials of the ligand molecules. Table 7, taken from the work cited[32], illustrates this relationship. The existence of this relationship indicates that there is donor–acceptor interaction in the complexes.

Table 7. Ionisation potentials and HFI constants for protons in the presence of DPPH.

Solvent	T_1/T_2	I, eV	a, s^{-1}	References
Chloroform	1.12	11.42		31
Acetonitrile	1.13	11.96		31
Dichloroethane	1.13	11.1		31
Dioxan	1.15	9.52		31
Benzene	1.16	9.24		31
1,3,5-Trifluorobenzene	1.18	9.15		31
Biphenyl (in CCl_4)	1.42	8.3	$>1.5\cdot10^5$	32
Naphthalene (in CCl_4)	2.15	8.1	$>3.3\cdot10^5$	32
Nitrobenzene	2.3	—	$1.1\cdot10^6$	32
Nitromethane	2.6	—	$3.5\cdot10^6$	32

Paramagnetic shifts were also observed in the last four solvents. The proton lines are displaced to strong fields, that is, there is negative spin density at the protons of the ligands in the complex with DPPH; this is apparently due to a mechanism involving σ–π configurational interaction of the electrons of the C–H bond with the positive spin density of the π-system of the ligand. For CH_3NO_2, the authors cited[32] propose localised interaction of the NO_2 group with the radical, the O–N–O group being similar to the allyl group: the π-electron spin density is positive at the oxygen atoms, and negative at the nitrogen atom; on the CH_3 group the spin density appears as a result of hyperconjugation with the unpaired electron of nitrogen and has the same sign. The HFI constants determined from the magnitudes of the paramagnetic shifts using Eqn. (5) are given in Table 7.

A number of studies have been carried out in solutions of stable nitroxide radicals of the type



The formation of complexes by radicals of this type with the molecules of water, alcohols, and acetic acid was observed by the EPR method[33]; it was shown that a hydrogen bond is formed between the radical and the solvent molecules with the participation of the unpaired electron. The energy of this bond amounts to 2–4 kcal mole^{-1} and the coordination number of the complex is $n = 1$.

The relaxation times of the protons of water in the presence of the nitroxide radical with X = CO have been measured[34]. The ratios T_1/T_2 for various concentrations of the radical are given in Table 8.

At low concentrations of the radicals, T_1/T_2 is much greater than unity, that is, the unpaired electron has a

finite density at the protons of the water molecules taking part in hydrogen bonding with the radicals.

Using the value $a = -0.56$ Oe obtained from the paramagnetic shifts (see p. 804) and $T_1/T_2 = 1.5$, we readily obtain the correlation time $\tau_e = 3 \times 10^{-10}$ s.

Table 8.

Concentration of radical, M	T_1/T_2	Concentration of radical, M	T_1/T_2
$5 \cdot 10^{-3}$	1.7	$5 \cdot 10^{-3}$	1.5
$7.5 \cdot 10^{-3}$	1.5	$7.5 \cdot 10^{-2}$	1.2
10^{-2}	1.6	10^{-1}	1.1
$2.5 \cdot 10^{-2}$	1.5	1.0	1.0

An interesting feature is that at high concentrations of the radical, when the frequency of electron exchange becomes equal to $\sim 10^{10}$ s^{-1}, the ratio T_1/T_2 gradually decreases and reaches unity at a concentration of 1 M. This behaviour of T_1/T_2 can be attributed to the fact that at high frequencies of exchange ω_{ex}, τ_{ex} becomes the correlation time of the isotropic HFI, and if $\tau_{ex} < \tau_e$, $\omega_S^2\tau_{ex}^2$ decreases with increase in concentration; as a result, there is a decrease in the contribution of the secular terms in T_2. This fact provides further proof of the manifestation of HFI at the protons of water in the complex with the radical; it also confirms that τ_e at concentrations in the region of 0.5 M (when the concentration dependence of T_2^{-1} begins to deviate from linearity) is comparable with τ_{ex}, that is, $\tau_e \simeq 10^{-10}$ s^{-1}; this shows good agreement with the value of τ_e calculated above from the values of the paramagnetic shift and the ratio T_1/T_2.

In the presence of the nitroxide radical with X = CH_2 (1 M) the ratio T_1/T_2 for the hydroxyl proton of methanol amounts to 1.23;[35] here, we should apparently observe the same picture as in aqueous solutions of the radicals.

A very interesting paper on the solvation of paramagnetic oxygen molecules in water and alcohols was recently published[36]. Only the dependence of T_1 for the protons in the pure solvents and in solutions saturated with oxygen on the field intensity (or ω_S) was measured. In pure water, T_1 was independent of ω_S; this means that $\omega_S^2\tau_C^2 \ll 1$, that is, the condition for strong narrowing is satisfied. In the presence of dissolved oxygen, T_1 depended on ω_S; this means that in the expression for T_1^{-1} there appears a second term which takes account of the contribution of the isotropic HFI, with correlation time $\tau_e < \tau_C$ and with $\omega_S^2\tau_S^2$ comparable with unity. It can readily be shown that for this example Eqn. (6) can be reduced to the form

$$T_1^{-1} = \alpha\tau_c + B\frac{\tau_e}{1+\omega_S^2\tau_e^2},$$

where α and B are constants, and τ_e and $\alpha\tau_C$ can readily be found by combining the expressions for T^{-1} with different ω_S values. For the complexes formed by oxygen with water molecules, the bond energy, determined from the temperature dependence of τ_e, was found to be 2.5 kcal mole^{-1}; τ_e is of the order of 10^{-11} s. In methanol, the dependence of T_1 on ω_S is very weak, that is, either the complexes formed by oxygen with the alcohol are weak (τ_e is small) or the constant a in the complex is small.

Thus the results of this work provide an elegant and convincing proof of the existence of complexes of oxygen with water molecules, in which there is delocalisation of the unpaired electrons of the oxygen over the atomic orbitals of the ligand.

The work examined above on the study of solvation using the ratio T_1/T_2 essentially exhausts the range of work carried out by this method in solutions of organic radicals. A disadvantage of this method is that it gives no information on the sign of the HFI constant in the complex; its advantage over methods which use measurement of paramagnetic shifts lies in the possibility of determining the kinetic characteristics of the complex—the correlation time τ_e and its temperature coefficient. Thus the two methods effectively supplement one another and give extensive information on the mechanism of the delocalisation of the unpaired electron in a complex; this is illustrated by the work examined above.

3. Dynamic Polarisation of Nuclei (Two-frequency Methods)

If we have two interacting spin systems—for example, electronic and nuclear—a change in the state of one spin system (at one resonance frequency) produces a change in the state of the other spin system; this change is detected at another resonance frequency. This is the essential feature of two-frequency methods of studying nuclear-nuclear and electronic-nuclear interactions. If we have a dipole interaction in an electron–nucleus system placed in a magnetic field, the component operators may bring about different transitions with a simultaneous change in the orientation of the electronic and nuclear spins, that is, with a change in the characteristic values of the z components of the spin of the electron M and the nucleus m. It can readily be seen from the form of the operator B that it brings about transitions $\Delta M = -\Delta m = \pm 1$ (flip-flop transitions), when there is simultaneous inversion of the electronic and nuclear spins in opposite directions. The operators C and D bring about transitions with $\Delta(M + m) = \pm 1$ (ordinary transitions of the electron or nucleus between their Zeeman levels), and the operators E and F induce transitions $\Delta M = \Delta m = \pm 1$ (flip-flip transitions) with simultaneous inversion of the spins of the electron and the nucleus in the same direction[37].

The Zeeman levels for the particular case of an electron and a proton and the populations of these levels are illustrated in Fig. 3 (it must be noted that for the electron $\gamma_e < 0$ and for the proton $\gamma_n > 0$); we have $N_-/N_+ = \exp(\hbar\gamma_e H/kT)$ and $n_+/n_- = \exp(\hbar\gamma_n H/kT)$.

With saturation of the electronic transitions there is an increase in the number of electron relaxation acts $+1/2 \rightarrow -1/2$; if only flip-flop transitions take place, the nuclear spins undergo inversion in the opposite direction $-1/2 \rightarrow +1/2$, that is, the population of the lower Zeeman level of the nuclear spin system increases sharply, with a corresponding increase in the NMR signal. For complete saturation of the electronic transitions $N_+ = N_-$ and $n_+/n_- = \exp(\hbar\gamma_e H/kT)$, that is, the populations of the nuclear states obey the Boltzmann relationship, but with the Boltzmann factor $\exp(\hbar\gamma_e H/kT)$ instead of $\exp(\hbar\gamma_n H/kT)$, which is observed for statistical equilibrium in the absence of EPR saturation. This means that for complete EPR saturation the effective gyromagnetic ratio of the nucleus γ_n is equal to the gyromagnetic ratio of the electron γ_e. This phenomenon of positive dynamic polarisation of nuclei for EPR saturation is known as the Overhauser effect. It is used in physics as a method of obtaining polarised

nuclei; in chemistry the Overhauser effect is important as a method of studying the nature and mechanism of electron–nuclear interactions in radicals and their complexes with ligands.

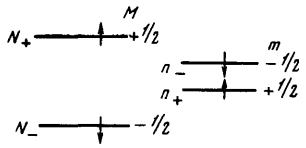


Figure 3. Scheme illustrating the Zeeman levels of the electron and the proton.

If only flip-flip transitions take place, the sign of the nuclear polarisation becomes negative. EPR saturation is then accompanied by an increase in the population of the upper Zeeman level of the nuclear spin system; relaxation of the nuclear spin is accompanied by the emission of the nuclear Zeeman frequency. This negative dynamic polarisation of nuclei is used in the production of microwave generators and amplifiers, or masers.

If we take account of all the transitions and solve the kinetic equations for the populations of the nuclear and electronic Zeeman levels, we obtain an equation relating the nuclear magnetisation $\langle I_z \rangle$ and the electronic magnetisation $\langle S_z \rangle$

$$\frac{\langle dI_z \rangle}{dt} = -\frac{1}{T_1^{II}}(\langle I_z \rangle - I_0) - \frac{1}{T_1^{IS}}(\langle S_z \rangle - S_0)$$

where I_0 and S_0 are the equilibrium values of $\langle I_z \rangle$ and $\langle S_z \rangle$ (in the absence of saturation); the constants T_1^{II} and T_1^{IS} are determined by the spectroscopic densities $J(\omega_I - \omega_S)$, $J(\omega_I)$, $J(\omega_I + \omega_S)$, and $J(\omega_I - \omega_S)$, $J(\omega_I + \omega_S)$ respectively. It can be seen from the equation that the polarisations of the spins I and S are related in such a way that a radiofrequency field with, for example, frequency ω_S, acting on $\langle S_z \rangle$, will also alter $\langle I_z \rangle$. Under steady-state conditions, $d\langle I_z \rangle / dt = 0$ and $\langle I_z \rangle - I_0 = \rho(\langle S_z \rangle - S_0)$, where $\rho = T_1^{IS}/T_1^{II}$.[30] The constant ρ is expressed in terms of the probabilities p, q, and r of the transitions produced by the operators B, C, D, E, and F respectively:

$$\rho = \frac{r - p}{r + 2q + p}.$$

The probabilities p, q, and r are calculated in the usual way via the correlation functions and spectroscopic densities. With the condition of strong narrowing, which is almost always satisfied in liquids, $p : q : r = 2 : 2 : 12$, so that $\rho = -1/2$, that is, for dipole–dipole interaction of the nuclei of the solvent with the unpaired electrons of the paramagnetic species we have negative dynamic polarisation of the nuclei.

The isotropic HFI operator produces only flip–flop transitions and if a contribution to the relaxation is made only by the isotropic HFI, we have $q = r = 0$ and $\rho = -1$, that is, in this instance there is positive polarisation, whose absolute magnitude is twice that of the negative polarisation corresponding to dipole–dipole interaction.

If both interactions make a contribution to the relaxation, ρ is a complex function of these contributions. Complete calculation of the spectroscopic densities for these interactions for $\omega_S^2 \tau_C^2 \ll 1$ leads to the following expression for ρ:[30]

$$\rho = \frac{1 - \tau_e/\sigma\tau_c\,(1 + \omega_s^2\tau_e^2)}{2 + \tau_e/\sigma\tau_c\,(1 + \omega_s^2\tau_e^2)}, \qquad (8)$$

where $\sigma = \hbar^2\gamma_n^2\gamma_e^2/r^6a^2$. It is clear that the magnitude and sign of the constant ρ contains all the "chemical" information regarding the nature of the interaction of the radical with the solvent molecules; it is usually determined experimentally from the dependence of the degree of polarisation on the level of EPR saturation (details can be found in a paper by Richards and White[38]). The magnitude and sign of ρ depend on many parameters—the magnetic field intensity, the isotropic HFI constant, viscosity, and temperature (via τ_C and τ_e).

Positive nuclear polarisation for protons was previously observed only in solutions of the alkali metals in ammonia ($\rho = -1$), in which the strongly solvated electron gives high values of a on the protons[39]. Recently, positive polarisation was observed on the protons of the t-butyl groups in tris-t-butylphenol in the presence of its radical tris-t-butylphenoxyl[40]. In the opinion of the authors cited[40], this is related to the fact that positive polarisation of these protons takes place in the radical, in which, as already noted (section I) there is considerable isotropic HFI at these protons. As a result of the exchange reaction of the radical with the phenol (see below), this polarisation appears in the phenol, and if the characteristic time of the reaction is less than the relaxation time of the protons in the molecule, this polarisation is preserved in the phenol and is detected.

An interesting feature is that in contrast to the situation for the protons of the t-butyl groups, the polarisation of the *meta*-protons in the same radical is negative, although the HFI on these protons is large ($a_H = 1.7$ Oe). This means that the contribution of the scalar relaxation is small, since there is no effective mechanism for the modulation of a (the corresponding spectroscopic densities are small).

This fact is of considerable interest in connection with the problem of the mechanism of delocalisation of the unpaired electron in the orbitals of the CH_3 groups in tris-t-butylphenoxyl. Since a necessary condition for positive polarisation is modulation of the HFI constant, and a mechanism for this modulation may be provided by internal rotation in the t-butyl groups, this means that the unpaired electron is delocalised in the t-butyl groups over the angular orbitals, that is, by a hyperconjugation mechanism. These considerations are also confirmed by data on the dynamic polarisation of ^{13}C nuclei (natural concentration) in the t-butyl groups of this radical—the sign of the polarisation is positive[41]‡.

In the presence of organic radicals it has been possible to observe the contribution of the isotropic HFI only in the polarisation of the fluorine nuclei in fluorine-containing solvents. Thus in solutions of DPPH in 1,3,5-trifluorobenzene[42], $\rho = 0.37$ (at the fluorine nuclei), that is, $-1 < \rho < 1/2$, indicating a contribution by the isotropic HFI to the polarisation of the fluorine nuclei.

‡ In principle, polarisation may be induced by the same mechanism by chemical reactions taking place with the formation of radicals. This was recently confirmed experimentally[60,61]. This is an extremely promising development from the viewpoint of kinetics and mechanism, and also in connection with the possibility of creating a "chemical" maser.

In fluorobenzene in the presence of DPPH, ρ has a value equal to approximately zero at 20°C, that is, the contributions of the dipole–dipole and isotropic interactions to the dynamic polarisation of fluorine are almost identical; with increase in temperature, however, the contribution of the isotropic interaction decreases, that is ρ increases[42]. This means that the temperature dependence of the correlation time τ_e is more marked than that for τ_c.

Eqn. (8) can be written

$$\rho = \frac{1-\alpha}{2+\alpha},$$

where

$$\alpha = \frac{\tau_e}{\sigma\tau_c}(1+\omega_s^2\tau_e^2)^{-1}$$

and

$$\ln\alpha = \ln\frac{\tau_e^0}{\sigma\tau_c^0} + \frac{e_e - e_c}{RT} - \ln(1+\omega_s^2\tau_e^2).$$

This equation was used by the authors cited[42] to calculate ϵ_e from the dependence of α on $1/T$; it shows satisfactory agreement with experiment. Using the value of ϵ_c found by Gutowsky and Tai[31] (ϵ_c = 2.5 kcal mole^{-1}), the authors cited[42] found that the energy of the bond in the complex formed by DPPH with fluorobenzene amounts to 3.3 kcal mole^{-1}.

Richards and coworkers[26,43] observed positive nuclear polarisation of fluorine in a number of fluorine-containing solvents—C_6F_6, *p*-difluorobenzene, CF_3–CCl_3, $CFCl_2$–CF_2Cl, fluorine-containing alcohols, perfluoroacetone, and hexafluoroethane—in the presence of DPPH, tris-t-butylphenoxyl, and semiquinone radicals. This shows that in the complexes formed by the fluorine-containing molecules with the radical there is strong isotropic HFI, associated with the appearance of spin density on the fluorine nuclei of the ligand.

The dynamic polarisation of ^{31}P nuclei in phosphites and phosphates in the presence of tris-t-butylphenoxyl was recently studied[44]; the sign of the polarisation is positive, that is, the radical also forms complexes with phosphorus-containing esters, in which the isotropic HFI at the phosphorus nucleus is large. The polarisation is greater in phosphites than in phosphates. The authors cited attribute this to the fact that in the phosphites the phosphorus atom has a free $3s^2$ pair, so that there is an increase in the isotropic HFI in the complex.

A large number of papers have been devoted to the dynamic polarisation of protons in the presence of organic radicals, but they are of slightly less interest from the viewpoint of "chemical" information. In most instances in these systems $\rho = 1/2$, that is, the main contribution to the polarisation is made by dipole–dipole interactions. These papers, however, contain a large amount of information on the correlation times τ_c and ϵ_c, characterising the intensity of the molecular Brownian movement in various liquids; this is of considerable interest for the kinetic theory of liquids[45,46].

Until now we have been considering those two-frequency methods in which EPR saturation at microwave frequency has led to changes in the populations of the Zeeman levels of the nuclear spin system and these changes have been detected at the NMR radiofrequency. At the present time, increasing use is being made of another version of the two-frequency method—electron–nuclear double resonance—for the study of organic radicals. The essential features are as follows. For saturation with a microwave frequency, the EPR signal decreases. If the radiofrequency is now altered slowly, it is found that at values corresponding to the resonance of a given type of nuclei, by flip–flop or flip–flip transitions, a change takes place in the populations of the electronic Zeeman levels and the EPR signal at this frequency also changes (it increases or decreases to a greater extent, depending on which transitions play the most important role). Thus in this instance detection takes place at the microwave frequency, and the NMR radiofrequency is used as a probe for the electron–nuclear interaction. This method, discovered by Feher[47], has been used successfully for a considerable time to study the structure of paramagnetic centres in crystals; only a few papers[48,49] have been devoted to the study of organic radicals in liquids. A significant advantage of double resonance is the considerable simplification of the EPR spectra and the high accuracy of the determination of the HFI constants. For example, in triphenylmethyl, which contains three kinds of magnetically non-equivalent hydrogen nuclei, the EPR spectrum consists of 196 lines of hyperfine structure, whereas the double resonance spectrum contains only six lines[49]; the double resonance spectrum of triphenylphenoxyl contains seven lines instead of 4050.[50] The most valuable feature of double resonance in radicals in single crystals, however, is that it makes it possible to determine the absolute signs of the hyperfine interaction constants. An example is provided by the determination of the signs of the HFI constants on the β-protons in the radical HOOC–$\dot{C}$H–CH_2COOH.[51]

III. NMR AND THE KINETICS OF RADICAL REACTIONS

In recent years the theory has been developed and NMR has been successfully applied, for the study of the kinetics of radical reactions, in particular electron exchange and radical substitution taking place with transfer of a hydrogen atom. The attractions of the NMR method for these purposes include not only the possibility of studying fast reactions (with rate constants of 10^8–10^9 litre mole^{-1} s^{-1}) but also, and this is most significant, the fact that this method makes it possible to study the kinetics of reactions taking place with zero heat change, that is, elementary reactions with the same initial and final states; it is extremely difficult to study the kinetics of these reactions by classical methods, although it is these reactions which are of greatest interest for the theory of reactivity. Another extremely important aspect is that it becomes possible in principle to study electronic interactions in the activated complex.

The use of the method is based on the broadening of the NMR signals from the nuclei in the molecules which are taking part in the exchange of electrons or hydrogen atoms:

$$P + D \overset{k}{\rightleftarrows} D + P \qquad (9)$$

where P is the paramagnetic species (ion or radical), and D is the diamagnetic ion or molecule. Each elementary act of this reaction leads to a change in the magnetic field acting on the resonance nuclei of the corresponding molecules, since as a result of this reaction these nuclei are found at one moment in the paramagnetic species, when they are acted on by the field of the unpaired electron, and at another moment in the diamagnetic molecule. Thus the nuclei are acted on by paramagnetic "pulses" whose intensity and frequency influence the shape and width of the NMR lines. To study the kinetics of these reactions it is possible to use the line width for any nucleus of a molecule taking part in the reaction, where there is an isotropic HFI.

In general, for reaction (9), an expression for the paramagnetic broadening of the NMR lines can be obtained either by solving Bloch's kinetic equations for the magnetisation or by means of relaxation matrices[52]

$$\Delta T_2^{-1} = \frac{f_P \tau_P a^2/4}{1 + f_D \tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1}}, \quad (10)$$

where ΔT_2^{-1} is the paramagnetic broadening; $\Delta T_2^{-1} = T_{2,PD}^{-1} - T_{2,D}^{-1}$, where $T_{2,PD}^{-1}$ and $T_{2,D}^{-1}$ are the widths of the NMR lines in the presence and absence of the paramagnetic species P; f_P and f_D the mole fractions of P and D; τ_P the lifetime of the paramagnetic species; T_{1e} the electronic longitudinal relaxation time; and a the isotropic HFI constant at the nuclei whose resonance is observed. Experimentally, it is possible to realise conditions under which Eqn. (10) is simplified. Two cases are known, described by the terms "strong pulse" and "weak pulse".

Let us examine the first—the strong pulse. For this to be realised, the following conditions are necessary.

Firstly, the lifetime of the paramagnetic species should be much shorter than the lifetime of the diamagnetic species, that is, $\tau_P \ll \tau_D$. Since $\tau_D = 1/k(P)$, and $\tau_P = 1/k(D)$, this condition requires that $(P) \ll (D)$; this is readily satisfied, and $f_D \simeq 1$.

Secondly, it is necessary that $\tau_P^2 a^2 \gg 1$. Since the frequency of precession of the nucleus in the field of the unpaired electron is equal to $a/2$, this nucleus comes out of phase with the other nuclei in the molecule D, if the paramagnetic "pulse" lasts longer than one period corresponding to the precession frequency a, that is, if $\tau_P \gg 1/a$. This means that either a or τ_P should be sufficiently large for the nuclei to come completely out of phase during the period for which the unpaired electron is in the molecule; the paramagnetic broadening on the nuclei will be the same and independent of a. For the same reason it is necessary that the electronic relaxation time or electronic exchange time $T_{1e} \gg 1/a$, that is, $T_{1e}^2 a^2 \gg 1$, so that all the nuclei are able to come out of phase before the electron alters its orientation. In this instance neither relaxation of the electron spin nor electron exchange influence the broadening. The last two conditions can be combined into one, namely, $a^2\tau^2 \gg 1$, where $1/\tau = 1/\tau_P + 1/T_e$. For the "strong pulse" case, the transverse relaxation time is determined essentially by τ_D, since $\tau_D \gg \tau_P$ and when time τ_D has elapsed (after D is converted into P) the nuclei come out of phase almost immediately. Since $a^2\tau^2 \gg 1$, the experimental criterion for realisation of the "strong pulse" case is preservation of the hyperfine structure of the EPR spectrum of the paramagnetic species.

The condition $a^2\tau^2 \gg 1$ may be satisfied, although the hyperfine structure is not observed, if $T_{1e} > T_{2e}$, where T_{1e} and T_{2e} are the longitudinal and transverse electronic relaxation times. This is due to the fact that the width of the EPR lines, determined by T_{2e}, may become greater than the splitting.

When these conditions are satisfied, Eqn. (10) becomes

$$\Delta T_2^{-1} = k(P)(D) \quad (11)$$

by means of which k can readily be found from the magnitude of the broadening and the known concentrations (P) and (D). Since the condition $\tau_P^2 a^2 \gg 1$ is most readily satisfied for large values of τ_P or small values of k, the "strong pulse" case corresponds to a slow reaction. This was first analysed by McConnell[53].

Let us now consider the second case—the "weak pulse" case—which is realised under the following conditions.

Firstly, as before, $\tau_D \gg \tau_P$. Secondly, $\tau_P^2 a^2 \ll 1$ or $\tau_P \ll 1/a$, that is, the lifetime of the paramagnetic species, during which the nuclei are exposed to the local field of the unpaired electron, is less than the period of the Larmor precession of the nucleus in this field, leading to its averaging and the production of a paramagnetic shift. A result of the reaction is modulation of the HFI constant and the consequent scalar relaxation, described above.

Here, a necessary condition is that $\tau_P \ll T_{1e}$, for if $\tau_P \gg T_{1e}$ the correlation time of the isotropic HFI becomes the electron spin relaxation time T_{1e}, which is not related to the reaction and the study of the kinetics of the reaction itself becomes meaningless.

If $T_{1e} \simeq \tau_P$, it is necessary to know T_{1e} in order to study the kinetics of the reaction. Since in time τ_P the nuclei with different values for the isotropic HFI constant a_i are able to come out of phase to different extents, the paramagnetic broadening is not the same for all nuclei and is determined by the quantity a_i^2. In this instance, $f_D\tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1} \ll 1$ and Eqn. (10) becomes

$$\Delta T_2^{-1} = \frac{1}{4}\frac{(P)}{(D)^2} a^2 k^{-1}, \quad (12)$$

from which it is possible to find k if we know a at the nuclei whose resonance is being observed. In contrast to the previous case, the broadening decreases with increase in temperature, since it is inversely proportional to the rate constant k. The condition $\tau_P^2 a^2 \ll 1$ is readily satisfied at small values of τ_P, that is, at large values of k, so that these conditions correspond to fast reaction or fast exchange; it was examined first by Bloembergen[29].

These are the conditions and chief characteristic features of the two extreme limits, which might be described respectively as the limits of deep low-frequency modulation and superficial high-frequency modulation.

The paramagnetic shift produced by reaction (9) has the form

$$\Delta H = -a f_P (\gamma_e/\gamma_n)(\gamma_e H/4kT)\left(1 + \frac{f_D\tau_P^2 a^2}{4}\right). \quad (13)$$

For $\tau_P^2 a^2 \ll 1$ ("weak pulse")

$$\Delta H = -a f_P (\gamma_e/\gamma_n)(\gamma_e H/4kT), \quad (14)$$

which coincides with the expression for the paramagnetic shift in polycrystalline radicals, where $f_P = 1$, Eqn. (5). Eqn. (14) is also used to determine the constants a from the paramagnetic shifts of a solvent in the presence of radicals forming complexes with the solvent (see section II).

The first report of the use of NMR in the kinetics of organic reactions appeared in 1956. Bruce and coworkers[54] measured the rate constant for electron transfer from tetramethyl-*p*-phenylenediamine to the corresponding Wurster's radical-cation in acetic acid at pH 3.2. In the presence of Wurster's cation, the NMR lines of the solvent (water, acetate ion) undergo very little broadening, whereas the lines of the ring and methyl protons of the reacting diamine undergo broadening equally strongly and in proportion to the concentration of the cation; this shows that the "strong pulse" case is realised, and the constant calculated from Eqn. (11) was found to be 2.5×10^4 litre mole^{-1} s^{-1}.

The kinetics of this reaction were recently studied in detail by the NMR method over a wide pH range in D_2O.[55] The original amine was taken in the form of its dihydrochloride, so that the reaction mixture contained equilibrium quantities of the dihydrochloride, the monohydrochloride, and the free base. The broadening of the lines was the same for the methyl and ring protons of the amine ("strong pulse"). The rate constants showed a marked dependence on pH, decreasing with decrease in pH; this

shows that the tendency to take part in electron transfer differs considerably for the base (the amine) and its salts (the mono- and di-hydrochlorides). If it is assumed that only the free base takes part in electron exchange with the cation-radical, it is possible to calculate the true rate constant for this bimolecular reaction; it was found that over the wide pH range 2.7–6.1, this constant does in fact remain constant and is equal to $(1.5 \pm 0.7) \times 10^8$ litre mole^{-1} s^{-1} at 20°C.

The conclusion that only the free base takes part in electron transfer is also confirmed by data obtained by Johnson[56], who studied the same reaction in acetonitrile, with all the amine in the form of the base. In contrast to the earlier work, where the "strong pulse" case was realised, the broadening of the methyl and ring protons of the amine in acetonitrile was found to be proportional to the square of the HFI constants at these protons (6.76 Oe and 1.97 Oe), and the rate constant determined from Eqn. (12) amounted to $\sim 2 \times 10^8$ litre mole^{-1} s^{-1}; this agrees with the true rate constant determined in the previous paper. Thus in acetonitrile, in which electron exchange takes place rapidly, the "weak pulse" case is realised. A similar difference in the broadening of the NMR lines of different protons was observed in diethyl-*p*-phenylenediamine in aprotonic solvents, and also in the di-cations of ethyl- and methyl-viologen in the presence of their paramagnetic mono-cations; here, the fast exchange case ("weak pulse") applies throughout[56].

An interesting example was observed in a study of the kinetics of electron transfer in *p*-xylene[21] in the presence of its anion-radicals, obtained by the reaction of *p*-xylene with potassium. Since the HFI constants *a* for the ring and methyl protons in the anion differ considerably (5.34 Oe and 0.08 Oe respectively), both cases are realised in electron exchange—"strong pulse" for the ring protons and "weak pulse" for the methyl protons. The broadening of the ring protons increases with increase in temperature, whereas the broadening of the methyl protons decreases—in accordance with Eqns. (11) and (12). For this particular case, Johnson[56] proposed a method for determining *k*, which does not require a knowledge of the concentration of paramagnetic species P. In actual fact, by combining Eqns. (11) and (12) for the broadening of the lines for different protons, one can immediately obtain *k* and the concentration of paramagnetic species (P).

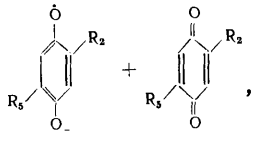
The following expression was obtained for the rate constant for electron transfer in the system formed by *p*-xylene and the *p*-xylene anion[21]:

$$k = 10^{12} \exp(-6200/RT) \text{ litre mole}^{-1} \text{ s}^{-1}.$$

These constants are much smaller than the constants obtained for the same reaction in the absence of potassium (when the anions are obtained by electrolysis). This shows that the constants given above relate to the slower exchange of *p*-xylene with an ion pair:

$$P^-K^+ + D \rightleftarrows D + P^-K^+ .$$

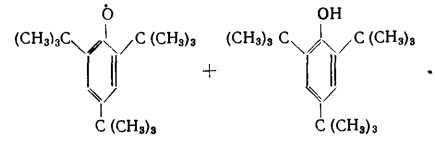
The rate constants for electron transfer in the quinone–semiquinone system



where $R_2 = -CH(CH_3)_2$ or $-OC_2H_5$, and $R_5 = H$ or OC_2H_5, were found to be close to 10^8 litre mole^{-1} s^{-1}.

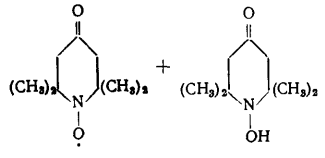
An anomalous ratio $T_1/T_2 > 100$ is observed at the α-proton in $-CH(CH_3)_2$ and at the methylene protons in $-OC_2H_5$; this anomaly may appear for the "weak pulse" case; the correlation time of the isotropic HFI—Eqn. (7)—becomes τ_P.[57]

Radical substitutions have been the subject of only one paper, by Kreilick and Weissman[58], who studied the kinetics of hydrogen atom transfer from tris-t-butylphenol to tris-t-butylphenoxyl:



The reaction was carried out in CCl_4 in the presence of $Si(CH_3)_4$ as internal standard. The NMR of a solution of the phenol in CCl_4 gives four lines: two from the protons of the non-equivalent *o*- and *p*-t-butyl groups and two from the *meta*-protons and the hydroxyl proton. With increase in the concentration of the radical, the lines for the t-butyl and *meta*-protons broaden to equal extents, in proportion to the concentration of radicals ("strong pulse"). The correction for the dipole–dipole electron–nuclear broadening was determined from the broadening of the tetramethylsilane protons; this correction was very small. The constant *k*, determined from Eqn. (11), amounted to 300 litre mole^{-1} s^{-1} at 30°C, and the activation energy for the reaction was 1.0 ± 0.5 kcal mole^{-1}.

In the paper cited, the correction for the dipole–dipole broadening was introduced wrongly (this is pointed out by the authors themselves), since the correlation time τ_C of the dipole–dipole interaction of the tetramethylsilane and phenol protons with the unpaired electron of the radical should be different. In our study of the same reaction[59], the dipole–dipole correction was determined from the broadening of the lines of tris-t-butylbenzene, for which τ_C should be very close to τ_C for tris-t-butylphenol; the constant *k* at 25°C was found to be 400 litre mole^{-1} s^{-1}, which is very close to the constant obtained by Kreilick and Weissman. Moreover, we determined the rate constant for the analogous reaction



from the broadening of the lines of the methyl protons: $k = 130$ litre mole^{-1} s^{-1} at 25°C; here the dipole–dipole correction was determined from the broadening of the lines of the methyl protons of the corresponding amine.

The behaviour of the NMR line of the hydroxyl proton is of greatest interest, since as a result of each act of the reaction, the initial and final states of this proton remain unchanged: it always remains in a diamagnetic molecule, with the exception of the activated complex. For the broadening of its NMR line we can use Eqn. (10), in which $f_P = f_{act}$—the mole fraction of the activated complexes; it can readily be shown that $f_{act} = k(P)\tau_{act}$—also τ_P becomes the lifetime of the activated complex τ_{act}, and *a* is equal to the HFI constant in this complex a_{act}. Then for $\tau_{act} T_1^{-1} \ll 1$ we have

$$\Delta T_2^{-1} = k(P) \frac{\tau_{act}^2 a_{act}^2/4}{1 + \tau_{act}^2 a_{act}^2/4} . \qquad (15)$$

In the paper by Kreilick and Weissman, this equation was used to determine τ_{act} with arbitrary assumptions regarding the magnitude of a_{act} (20 Oe). These estimates of τ_{act} ($\sim 10^{-9}$ s) are hardly meaningful; it is more appropriate to determine a_{act} by giving τ_{act} a definite reasonable value.

There are, of course, fundamental difficulties in this approach. It is necessary first of all that the rate constant k be sufficiently high (fast reactions). Moreover, the formation of the activated complex may be preceded by the formation of ordinary donor–acceptor complexes (for example, by hydrogen bonding), so that a contribution to ΔT_2^{-1} will be made not only by states close to the top of the potential barrier for the reaction but also by these donor–acceptor complexes (this situation apparently was observed in the work of Kreilick and Weissman[58]). Moreover, formula (15) does not take account of the anisotropic HFI, although this interaction itself will produce additional broadening in states lying close to the top of the barrier. All these features make it difficult at present to determine the HFI constants in an activated complex.

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Methods of Thermokinetic Analysis of Chemical Reactions

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The theoretical foundations of the thermokinetic method of investigating chemical reactions are discussed. An analysis is made of the method as applied to the kinetics of adiabatic and non-adiabatic reactions, including heterogeneous catalysis. Methods of calculating kinetic parameters from experimental thermokinetic curves by different versions of the method are discussed. New ways of applying the thermokinetic method to studies of heterogeneous catalysis in flow systems are proposed. Examples are given of the use of the thermokinetic method in studies of a wide range of chemical reactions. The advantages of the thermokinetic method are briefly assessed. 50 references.

CONTENTS

I.	Introduction	812
II.	Homogeneous reactions	812
III.	Heterogeneous exothermic reactions	815
IV.	Special features of thermokinetic methods for the study of fast reactions	815
V.	Non-stationary thermokinetic methods	816
VI.	Examples of the use of thermokinetic methods	817
VII.	Advantages of thermokinetic methods	817

I. INTRODUCTION

Whenever possible, kinetic measurements are made under isothermal conditions: this tendency is fully justifiable, since isothermal kinetics are usually easy to treat mathematically.

However, there is a large group of reactions which cannot be made to take place isothermally because of the large thermal effects involved. These include reactions in media of low thermal conductivity and fast reactions with high initial concentrations of reactant and leading to explosion or ignition.

Most of the industrially important polymerisation and polycondensation reactions are strongly exothermic and usually proceed with appreciable self-heating. A number of variants of the thermometric method, based on measurements of temperature as a function of time, have been proposed for kinetic studies of reactions of this type.

There are also reactions (for example, the formation of condensation oligomers) which can only be taken to completion by gradually raising the temperature. These reactions can be investigated by thermokinetic methods, based on programmed heating[1].

Theoretical and experimental results relating to the thermokinetic method are scattered among journals for different fields, depending on the type of reaction being studied. Hence, there was a need for a review article and for a systematisation of existing methods.

The present article is devoted to an analysis of methods of treating experimental thermokinetic data so as to extract from the data the variation with time of the extent of reaction, the rate constants, and the activation energies. We shall review the most important publications up to 1968, and we shall briefly characterise the thermal regime and the current applications of thermokinetic methods. We shall be little concerned with the design of detectors used in the thermokinetic method, of calorimeters, and with other experimental problems, because they are exhaustively discussed in a number of monographs[2-5].

II. HOMOGENEOUS REACTIONS

1. Adiabatic Regime

The simplest relationship between ΔT and the extent of reaction is obtained with adiabatic reactors, and also with pseudo-adiabatic calorimeters provided with automatic compensation for the heat losses which occur when a temperature difference arises between the wall of the reaction vessel and the mass of reactant[6].

In these instances, as may be shown from the heat balance equation for an adiabatic reaction, the relationship between the conversion α and the temperature T at time t is of the form

$$\alpha = \frac{T - T_0}{T_{ad} - T_0} = \frac{\Delta T}{\Delta T_{ad}} \qquad (1)$$

where

$$\Delta T_{ad} = T_{ad} - T_0 = \frac{Q_p}{\bar{C}_p}$$

where Q_p is the heat of reaction, cal mole^{-1}; $\bar{C}_p$ the mean heat capacity of the reaction mixture, cal mole^{-1} deg^{-1}; and T_0 the initial temperature of the surrounding medium.

In the absence of reliable values for Q_p and $\bar{C}_p$, the experimenter can determine only the conversion α_{max}, corresponding to the maximal observed value of ΔT. Then,

$$\Delta T_{ad} = \Delta T_{max}/\alpha_{max}.$$

The steepness of the experimental plots of ΔT against t depends, as can readily be seen, not only on the rate constant at $T = T_0$ but also on the activation energy E. This follows from the kinetic equation for an adiabatic reaction[7]:

$$\frac{dT}{dt} = k_0 (T_{ad} - T)^n \exp(-E/RT) \left(\frac{x_0}{T_{ad} - T_0}\right)^{n-1}, \qquad (2)$$

or

$$\frac{dT}{dt} = k_0 \left(\frac{C_p}{Q_p}\right)^{n-1} (T_{ad} - T)^n \exp\left(-\frac{E}{RT}\right), \qquad (2a)$$

where n is the order of the reaction, k_0 the pre-exponential factor, and x_0 is the initial concentration of reactant.

An expression for the activation energy can be obtained from the logarithmic form of this equation[6,8,9]. The activation energy is then given by the slope of the linear plots of $\ln \frac{dT/dt}{(T - T_0)^n}$ against $1/T$ or $\ln \frac{dT}{dt}$ against $1/T$, which is equal to $-E/R$.

It should be noted that the integral form of Eqn. (2) cannot be expressed[10] in simple functions in the general case, even with $n = 1$.

Livshits suggested[11] that the activation energy of non-isothermal (including adiabatic) reactions could be determined from the position of the point of inflection of experimental plots of T against t. This point, corresponding to maximal reaction rate, is reached when the "temperature" acceleration (or retardation) of the adiabatic reaction is fully compensated by the "concentration" retardation (or acceleration).

Table 1. Types of non-isothermal reaction with extreme dependence of rate upon time.

Type of reaction and $\varphi(\alpha)$	$\frac{d\varphi(\alpha)}{dt}$	Thermal effect, Q_p	Thermal regime up to point of inflection (dT/dt)
nth order reaction, $(1-\alpha)^n$ with $n > 0$*	<0	>0	>0
nth order reaction with retardation, $(1-\alpha)^n$ with n <0*	>0	<0	<0
Autocatalytic first-order reaction, $(1-\alpha)\alpha$ with $0.5 < \alpha < 1$	<0	>0	>0
Ditto, $(1-\alpha)\alpha$, with $0.5 > \alpha > 0$	>0	<0	<0
α^n; $n > 0$	>0	<0	<0
α^n; $n < 0$	<0	>0	>0
First-order reaction with retardation, $(1-\alpha)/\alpha$	<0	>0	>0

* With zero-order reactions $n = 0$, and the rate of non-isothermal reaction continuously increases ($Q_p > 0$) or decreases ($Q_p < 0$). In this case the activation energy is determined by the slope of the linear plot $\ln(dT/dt) = f(1/T)$, which is equal to $-E/R$.

To analyse this method, we note that the kinetic equation of an adiabatic reaction can be expressed in the general form;

$$\frac{d\alpha}{dt} = k_0 \varphi(\alpha) f(T). \qquad (3)$$

The quantity $d\alpha/dt$ goes through a maximum if the time changes of $\varphi(\alpha)$ and $f(T)$ are equal and opposite. It can be shown that this condition is realised in a number of instances, listed in Table 1.

Since $f(T) = \exp(-E/RT)$, and k_0 is not a function of T, E can be determined at the instant corresponding to the point of inflection (that is, $d^2\alpha/dt^2 = 0$) if the form of $\varphi(\alpha)$ is known.

Hence, by differentiating Eqn. (3) and equating the second differential to zero, a direct relationship is obtained between the activation energy and the temperature T_i of the reaction mixture at the point of inflection of the thermokinetic curve. Expressions for the activation energy of reactions obeying different kinetic laws are given in Table 2.

2. Non-adiabatic Non-isothermal Reactions

The heat balance equation for a non-isothermal reaction is of the form

$$m_0 Q_p \frac{d\alpha}{dt} - H\frac{dT}{dt} - \beta(T - T_0) = 0 \qquad (4)$$

where H is the effective heat capacity of the system, cal deg^{-1}; β the heat transmission coefficient, cal deg^{-1} s^{-1}; and m_0 the number of moles of reactant.

Table 2. Activation energy of various adiabatic reactions.

Kinetic law	Expression for the activation energy	Kinetic law	Expression for the activation energy
$(1-\alpha)^n$ $n \neq 0$	$E = \frac{nRT_i^2}{\Delta T_{ad} - \Delta T_i}$	α^n; $n \neq 0$	$E = -\frac{nRT_i^2}{\Delta T_i}$
$(1-\alpha)\alpha$	$E = \frac{RT_i^2(2\Delta T_i - \Delta T_{ad})}{\Delta T_i (\Delta T_{ad} - \Delta T_i)}$	$(1-\alpha)/\alpha$	$E = \frac{RT_i^2 \Delta T_{ad}}{\Delta T_i (\Delta T_{ad} - \Delta T_i)}$

Integration of Eqn. (4) for the initial conditions $\alpha = 0$, $t = 0$, and $T = T_0$ gives

$$m_0 Q_p \alpha = \int_0^T \beta(T - T_0)\,dt + H(T - T_0). \qquad (5)$$

For the condition[12,13] $T_0 = \text{const}$ the T–t curve can be transformed into an α–t curve by graphical integration once H and β have been evaluated. For relatively small values of ΔT it can be assumed that β and H are constant.

In the more general case we can assume

$$\beta = \beta_0 T_0^l; \quad H = H_0 + a(T - T_0),$$

where β_0, H_0, l, and a are constant.

Using Newton's law of cooling it can be shown[12] that the extent of conversion at time t is given by

$$\alpha = \frac{\int_t^\infty (T - T_0)\,dt + \int_0^t (T - T_0)\,dt}{\int_0^\infty (T - T_0)\,dt}. \qquad (6)$$

The integral $\int_t^\infty (T - T_0)dt$ is evaluated from the cooling curve by measuring the area under the curve between T and T_0. The second integral is equal to the area under the thermokinetic curve between 0 and t, and the integral in the denominator is equal to the area under the whole of the experimental curve, including the cooling period, up to the temperature T_0.

Evreinov and Entelis[13] used this method[12] in a modified form, which required the determination of β and H using Eqn. (5).

The β coefficient is evaluated from the cooling of copper specimens[14] or by electrical heating to the temperature T_{lim} at which the rate of heat evolution is equal to the rate of heat loss. Hence

$$\beta = \frac{0.2390\,N}{T_{lim} - T_0},$$

where N is the power dissipation of the heater in joules.

Also, the value of H/β, equal to

$$\frac{\int_t^\infty (T - T_0)\,dt}{T - T_0}$$

is obtained from the cooling curve. It is important to note that separate determination of H and β is not necessary: the first integral in the numerator of Eqn. (6) can be replaced by $H/\beta(T - T_0)$.

This type of treatment can be used as long as $T_0 = \text{const}$. If on the other hand the reaction is carried out under programmed heating, the quantity T_0 in Eqn. (6) must be replaced by the temperature of the surroundings for which the function $(T - T_0)$ is a maximum[15].

Methods of integration of non-isothermal kinetic equations with arbitrary temperature laws are given by Emanuel' and Knorre[16].

The more complicated case when the effective activation energy varies with extent of conversion has also been considered[14,17]. In this case, the functions $T = f(\alpha)$ and $\frac{d\alpha}{dt} = \varphi(\alpha)$ are obtained from Eqn. (6) and by graphical differentiation of the experimental T–t curve. The variation of the non-isothermal rate with reciprocal temperature is then determined for a number of values of α. Hence, using the equation $\frac{d\alpha}{dt} = k_0 \exp\left[-\frac{E(\alpha)}{RT}\right]\varphi(\alpha)$, the activation energy can be evaluated for the chosen values of α.

The non-isothermal rate is related to the isothermal rate of reaction at temperature $T = T_*$ by the equation

$$\left(\frac{d\alpha}{dt}\right)_{\substack{\text{isot}\\ T=T_*}} = \left(\frac{d\alpha}{dt}\right)_T \exp\left[\left(E/R\left(\frac{1}{T} - \frac{1}{T_*}\right)\right)\right]. \qquad (7)$$

An original method of treating thermokinetic data has been described by Korolev and coworkers[18]. Since the most commonly used reaction vessels are cylindrical, these authors considered the heat balance equation for an infinite cylinder of radius r:

$$\rho C \frac{dT}{dt} = \lambda\left(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dt}\right) + q(t)\,, \qquad (8)$$

where $q(t)$ is the rate of heat evolution, ρ is the density, λ is the thermal conductivity, and C is the heat capacity.

Eqn. (8) can readily be solved by a Laplace transform. Putting

$$\bar{z} = \int_0^\infty e^{-pt} T\,dt$$

and

$$\bar{q}(p) = \int_0^\infty q(t) e^{-pt}\,dt$$

and integrating Eqn. (8) multiplied by e^{-pt} between the limits $0 < t < \infty$, we obtain

$$C p\bar{z} = \lambda\left(\frac{d^2z}{dr^2} + \frac{1}{r}\frac{dz}{dr}\right) + \bar{q}(p)\,. \qquad (9)$$

The solution which satisfies the condition of symmetry with respect to $z\frac{dz}{dt}$ at $r = 0$ is a Bessel function of the first kind, of purely imaginary argument. Carrying out the series expansion, and after some transformations, we obtain

$$q(t) = \frac{4\lambda}{r_0^2}\left(T + \frac{r_0^2}{4} t_r \frac{dT}{dt}\right) \qquad (10)$$

where t_r (the relaxation time) is of the order of several minutes, and can be determined experimentally from the cooling and heating curves of the reaction mixture.

When applied to an adiabatic process, Eqn. (8) takes the form

$$q(t) \simeq \rho C \frac{dT}{dt}\,. \qquad (11)$$

In the proposed method[18], the portions of the thermokinetic curve for which $dT/dt = \text{const}$ are analysed. Under these conditions the reaction rate w is

$$w = \frac{dT}{dt} \cdot \frac{\bar{C}_p}{Q_p}\,.$$

If the rate of heat removal is equal to the rate of heat evolution (isothermal process), Eqn. (10) takes the form

$$q(t) = \frac{4\lambda}{r_0^2} T\,. \qquad (12)$$

In the case of a non-isothermal, non-adiabatic process the quantity $\frac{\rho C}{\lambda} r_0^2$ needed for the calculation is evaluated from the cooling rate of the reaction mixture from temperature T to T_0. Thus for a cylinder,

$$T = T_0 \exp\left(-\frac{\mu_1^2 \chi t}{r_0^2}\rho C\right) \qquad (13)$$

where μ_1 is the first root of the zero order Bessel function of the first kind ($\mu_1 = 2.401$).

Since the temperature [difference] falls by a factor of e in time t_r,

$$t_r = \frac{\mu_1^2 \lambda}{r_0^2 \rho C} = 1,$$

whence the desired quantity is

$$\frac{\rho C}{\lambda} r_0^2 = \mu_1^2 t_r\,.$$

In another group of methods of thermokinetic analysis of reactions, the heat evolution in the reaction mixture is reproduced by the application of current pulses of known power.

The design proposed by Skuratov and coworkers[19] is based on a double calorimeter, with cells of identical heat capacity. Current pulses of power equivalent to the rate of heat evolution in the working cell are applied to the reference cell. The kinetic curve is a plot of the square of the current in the reference cell against time. The area under the kinetic curve, multiplied by the appropriate proportionality factor, is a measure of the total heat evolution during the experiment.

The automatic calorimeter used by Anderson for emulsion polymerisation studies[20] is even more convenient. This calorimeter operates on the following principle. The adiabatic heating produced by the reaction and measured by a sensitive thermocouple is converted into electrical power, which is applied to the reactor in the form of pulses and measured by a wattmeter. The power of the pulses is automatically controlled at the level corresponding to constant total rate of heat evolution, that is, to the difference between the power in the absence of chemical reaction and the rate of thermochemical heat evolution. Special calibration is not needed to calculate the conversion at a given instant and the heat of polymerisation, since a power of 1 W is equivalent to a rate of heat evolution of 0.2390 cal s^{-1}.

III. HETEROGENEOUS EXOTHERMIC REACTIONS

The thermal regime of heterogeneous exothermic reactions was first discussed by Frank-Kamenetskii[21]. Depending on the rate of removal of heat, two stable temperature regimes were shown to be possible: the lower in the activation-controlled and the upper in the diffusion-controlled region. The steady-state heating of the surface in the upper regime can be used to evaluate the kinetic parameters.

The critical condition[21] leading to ignition for a first-order surface reaction is of the general form

$$\delta_{crit.} = \theta^2 e^{\theta} \tag{14}$$

and

$$\nu = e^{-\theta}(\theta - 1) \tag{15}$$

where

$$\delta = \frac{Q_p}{\beta}\frac{E}{RT_0^2}k_0 \exp(-E/RT_0)\, x_v$$

$$\theta = \frac{E}{RT_0^2}(T - T_0)$$

$$\nu = \frac{k_0 \exp(-E/RT_0)}{\gamma}.$$

Here x_v is the molar concentration of reactant in the bulk, γ is the mass transfer coefficient, defined by the expression

$$\gamma = \frac{(Nu)D}{d}$$

where (Nu) is the Nusselt criterion, D is the diffusion coefficient of the reactant, and d is the characteristic linear dimension of the system.

Rozovskii and coworkers have shown that the kinetic parameters of heterogeneous reactions of zero[22] and non-zero[23] order can be determined from the critical ignition condition.

For a zero-order reaction the critical ignition condition has the form

$$\delta_{crit.} = \frac{Q_p k_0 \exp(-E/RT_0')\, E}{\beta' R (T_0')^2}, \tag{16}$$

where the primes denote the values of the parameters corresponding to the onset of ignition.

By experimenting with different heat evolution conditions (through changes in linear velocity, which in turn produce a change in the ignition temperature T_0'), the following relationship between T_0 and δ_{crit} can be obtained:

$$\frac{\beta'_{(1)}\delta_{crit\,(1)}(T'_{0(1)})^2}{\beta'_{(2)}\delta_{crit\,(2)}(T'_{0(2)})^2} = \exp E/R\,(T'_{0(1)} - T'_{0(2)}). \tag{17}$$

Taking logarithms, and ignoring the term $\ln \frac{\delta_{crit(1)}}{\delta_{crit(2)}}$, we arrive at an expression for the activation energy involving only the ignition temperatures and the ratio of the heat transmission coefficients, which can be replaced by the ratio of the linear velocities raised to the power $s = 0.65$:

$$E = \frac{RT'_{0(1)}T'_{0(2)}\left(\ln\frac{\beta'_1}{\beta'_2} + 2\ln\frac{T'_{0(1)}}{T'_{0(2)}}\right)}{T'_{0(1)} - T'_{0(2)}} \tag{18}$$

(where the numbers in brackets refer to the number of the experiment). The rate constants at the ignition temperature are calculated by the formula

$$k = \frac{\delta_{crit}\beta' R (T_0')^2}{Q_p E}. \tag{19}$$

The quantity δ_{crit} is evaluated by one of the approximate formulae as a function of the parameter $b = \frac{RT_0}{E}$:

$$\delta_{crit} \simeq \frac{1+b}{e} \quad \text{or} \quad \delta_{crit} \simeq \frac{1+b+b^2}{e}.$$

The rate constants at any other temperature T are calculated by the formula

$$k_T = k_{T_0} e^{\frac{E(T-T_0)}{RTT_0}}$$

which is equivalent to Eqn. (7).

If the order of the reaction is not zero, the expression for the activation energy from the results of two experiments retains the form of Eqn. (18), but the pre-exponential factor is found from the equation

$$f(x_{i\,surf})\,k_0 = \frac{\delta'_{crit}\beta' k (T_0')^2}{Q_p E \exp(-E/RT_0')} \tag{20}$$

and the order n of the reaction with respect to the ith component is found from the variation of T_0' with $x_{i,surf}$ according to the equation

$$\lg \delta_{crit} + 2\lg T_0' + \frac{E}{4.575\,T_0'} = n_i \lg x_{i,surf} + A,$$

where A is a constant.

All the formulae used in this Section have been derived from the heat balance equation

$$\beta(T - T_0) = Q_p k_0 \exp(-E/RT) f(x_{i,surf}),$$

where $i = 0, 1, 2$.

It must be stressed that only the critical ignition temperature depends on the value of the heat transmission coefficient, which varies with the flow velocity. However, the steady state heating of the surface is independent of the gas flow velocity, as shown by Buben for the catalytic oxidation of hydrogen and ammonia on platinum[24].

In conclusion, we note that the thermokinetic methods of investigation of heterogeneous catalytic reactions lead to equations of the same mathematical form as those obtained for homogeneous processes. However, in the latter case one makes experimental plots of T against t, whereas in catalytic reactions the steady state heating of the surface at a particular point is observed as a function of the position of that point along the layer of catalyst.

It is evident that a definite contact time and extent of conversion must correspond to each cross-section of the catalyst in an integral reactor once a steady state is established. Thus, having determined the temperature distribution (in a uniform thermal field from the electric heater) along the catalyst column, the required kinetic parameters can be calculated from the formula given in Section II.

IV. SPECIAL FEATURES OF THERMOKINETIC METHODS FOR THE STUDY OF FAST REACTIONS

When applied to fast reactions, in which the half-life $\tau_{1/2}$ is of the order of 1 s or less, thermokinetic methods exhibit some specific features both in apparatus design and in the significance of the mathematical equipment.

We shall briefly discuss the thermometric methods of monitoring fast reactions, originally put forward in both a static and a flow variant.

In the first variant[25], the gas mixture in the reaction vessel is irradiated through a special window with ultraviolet light capable of initiating the reaction and of specific

intensity I_0 at the entry window. The absorption of light by the gas creates an intensity gradient in the vessel, and therefore the rate of thermochemical heat evolution decreases with increasing distance from the entry window. With a finite rate of heat transfer over the cross-section of the reactor, an easily detectable temperature gradient arises. An expression relating the temperature rise ΔT in the central zone of the reactor to the extinction coefficient ϵ and to the distance X from the window for an initial pressure P can easily be obtained from the heat balance condition:

$$\Delta T = \frac{I_0 h\nu\,[1-\exp(-\varepsilon X)]}{\lambda\varepsilon} \qquad (21)$$

where h is Planck's constant, ν is the frequency of the light used to initiate the reaction, λ is the thermal conductivity of the gas. A modification of the static variant, known as the thermal maximum method, has been developed for fast liquid-phase reactions.

In this method[26] a bulb containing one of the reactants is broken in a solution of the second reactant under standard conditions of fast stirring. If the reaction is exothermic, we observe a temperature rise determined by the value of the rate constant and by the efficiency of the heat exchange. This rise goes through a maximum, with time, if the order of the reaction differs from zero. The rate constant k_1 for a first-order reaction† is calculated from the equation[26]

$$\frac{\Delta T_{max}}{\Delta T_{ad}} = (k_1/k_2)^{\frac{k_2}{k_2-k_1}} \qquad (22)$$

where the cooling constant k_2 is defined by Newton's law

$$-\frac{dT}{d\tau} = k_2(T-T_0). \qquad (23)$$

If the heat of the reaction is not known, the adiabatic heating is obtained by measuring ΔT_{max} for a series of increasing concentrations of the first reactant and extrapolating to infinity. The rates of reactions with $\tau_{1/2}$ of the order of 0.2 s can be studied by this method[27].

The flow variant of the method is applicable both to liquid-phase[28] and to gas-phase[29] reactions: it is usually called the continuous flow method.

In the method developed by Roughton[28]‡ two streams of liquid reactants moving with a linear velocity of the order of metres per second are efficiently mixed and led into a capillary provided with a sensitive thermocouple whose junction can be moved controllably. Under the given conditions the reaction proceeds adiabatically§. Hence, the temperature rise (of the order of 0.2–0.3 deg) can easily be correlated with the extent of conversion. The variation of the conversion along the length of the capillary allows the rate constant to be determined to a reproducibility of ±7% at the lowest values of $\tau_{1/2}$ investigated (~ 0.1 s). When the flow method is applied to gas-phase reactions, substantial changes are necessary not only in the dimension of the apparatus and in the linear velocity, but also in the method of treatment of the results of the measurements: this is because of the non-adiabaticity of the process and of the need to use heat transfer equations in partial differential form (Laplace transform)[29].

† For a second-order reaction the equation involves complex functions.

‡ Sometimes wrongly transliterated in Russian as 'Роутон'.

§ Control experiments must be made to test whether the heat of mixing of the reactants is zero.

V. NON-STATIONARY THERMOKINETIC METHODS

Non-stationary kinetic methods are used when the number of kinetic constants to be determined is greater than the number of kinetic equations which can be written in the quasi-stationary approximation. We shall discuss the application of non-stationary thermokinetic methods by considering two examples: radical polymerisation and enzyme catalysis with Michaelis–Menten kinetics.

1. Radical Polymerisation of Vinyl Monomers

According to the kinetic equations for radical polymerisation, the rate of decrease of the monomer concentration is

$$-\frac{d[M]}{dt} = w_i^{1/2}\frac{k_p}{k_t^{1/2}}[M] \qquad (24)$$

where [M] is the monomer concentration, w_i is the rate of initiation, and k_p and k_t are the rate constants for chain propagation and chain termination respectively.

As can be seen from Eqn. (24), a study of the stationary radical polymerisation kinetics can only lead to a combination of the k_p and k_t constants ($k_p/k_t^{1/2}$).

Bengough and Melville[30] developed an inertia-free method involving measurements of the adiabatic heating of the mixture undergoing polymerisation during the initial period of the reaction under continuous illumination (photoinitiation), and calculation of the mean lifetime τ of the radicals. The extent of conversion at time t after the beginning of irradiation such that $t \gg \tau$ (in practice, $t > 5\tau$) is given by the expression

$$\alpha = \frac{\Delta T}{\Delta T_{ad}} = \frac{k_p}{k_t}\left(\frac{t}{\tau} - \ln 2\right). \qquad (25)$$

The quantity $\tau \ln 2$, and hence τ, is evaluated from the intercept of the linear plot of α against t (of slope $k_p/k_t\tau$) on the ordinate axis. From a knowledge of k_p/k_t and $k_p/k_t^{1/2}$, the two kinetic constants can be evaluated separately. One advantage of this method is the possibility of measuring conversions of the order of 10^{-4} mol.%.

Bagdasar'yan and Revzin[31] developed an original non-stationary kinetic method of determining k_p and k_t by observing the change in the adiabatic temperature rise accompanying a sudden decrease in the intensity of the irradiation responsible for initiation after a steady rate of polymerisation has been set up (background initiation method), In this method, the steady-state rate before and after the decrease in the rate of initiation must be known, as well as ΔT_{ad}. Thus, the non-stationary kinetic method can be used both in the early stages and in the late stages of a polymerisation reaction.

2. Enzyme Catalysis

The classical scheme of enzyme catalysis includes the formation of an intermediate enzyme–substrate (ES) complex, which subsequently decomposes with formation of the product P and can also partially dissociate into the starting components:

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftarrows}} ES \xrightarrow{k_2} E + P, \text{ with } k_{+1} \gg k_2.$$

By the conventional methods[32], only k_2 and the Michaelis constant K_m can be determined:

$$K_m = \frac{k_{-1} + k_2}{k_{+1}}.$$

By using low-inertia (including thermometric) methods of monitoring the reaction, the continuous flow method can detect the formation of the enzyme–substrate complex when the reaction leading to product formation is in a non-stationary (accelerating) regime. By extrapolating the linear (stationary) portion of the kinetic curve to the time axis, the mean lifetime τ of the enzyme–substrate complex can be determined. Knowing τ and the initial concentration of the substrate $[S_0]$, we can determine k_{+1} from the equation

$$\tau = \frac{1}{k_{+1}[S]_0},$$

and hence arrive at k_{-1} from the value of K_m.[33]

Another variant of the treatment of the experimental data, proposed by Roughton[34], yields the product $k_{+2}k_2$ from the curve for product accumulation during the non-stationary period.

To conclude this section, we note that the temperature jump method proposed by Eigen[35], which can be applied to systems at equilibrium, is sometimes classified among the non-stationary thermokinetic methods. The method relies on the practically instantaneous (10^{-6}–10^{-7} s) rise in temperature by 10–12 deg obtained by discharging a high-voltage condenser or by a laser flash, followed by observation of the relaxation of the system, that is, its approach to a new equilibrium. The method has also been applied to enzyme reactions, but even in the case of unimolecular reactions the measured relaxation time is a measure only of the sum of the rate constants for the forward and the reverse reaction.

VI. EXAMPLES OF THE USE OF THERMOKINETIC METHODS

Thermokinetic methods have been used to study the kinetics of a number of liquid-phase reactions (hydrolysis of esters[12,26], polycondensation of diacyl chlorides and glycols[13], polymerisation of styrene[15], alkene oxides[36], ethylenediamine[50], and oligoacrylates[37] in bulk). The polymerisation kinetics of styrene have been studied[20] by compensation calorimetry.

Thermokinetic studies of fast gas reactions include the photochemical dissociation of ethylene[25] and the reaction of boron trifluoride with aliphatic amines[29].

The adiabatic nature of thermal explosion and thermal ignition was established by Semenov[40], and the use of the adiabatic regime for studying these reactions has been discussed in monographs by Zel'dovich and Voevodskii[7], Frank-Kamenetskii[21], and Kondrat'ev[41]. A great deal of work has been devoted to the application of thermokinetic methods in studies of topochemical reactions (thermal decomposition of inorganic compounds, using differential thermography[8], decomposition of explosives[6,42], and thermal degradation of polymers[43]). The kinetics of various heterogeneous processes (adsorption, dissolution) have been investigated calorimetrically[2]. Critical ignition conditions have been used to study the kinetics of a heterogeneous catalytic reaction (the synthesis of alcohols from CO and H_2[44]).

The application of fast thermokinetic methods has been described in conjunction with the hydration of acetaldehyde[27], the preparation of polyamides[45] and polyesters[46], etc. Non-stationary thermokinetic methods have been used to study the polymerisation of vinyl acetate, acrylates[30], and oligoacrylates[47]. The kinetics of the formation of the enzyme–substrate complex in the cataly is of ribonuclease[58] and of chymotrypsin[49] have bee investigated by the temperature step method.

There can be no doubt that the number of investigations by thermokinetic methods will increase rapidly, in parallel with advances in the experimental techniques of this rapidly developing branch of chemical kinetics.

VII. ADVANTAGES OF THERMOKINETIC METHODS

Thermokinetic methods have unique advantages in the study of the kinetics of strongly exothermic reactions, in which isothermal conditions cannot be maintained, and of reactions in highly viscous media, which preclude effective stirring. In most of the variants of the thermokinetic method the whole of the kinetic curve can be obtained in a single experiment. The use of rising temperature conditions for the reaction (by exothermic self-heating or by programmed heating) enables the kinetics to be studied at extreme stages of the reaction, which is not always possible under isothermal conditions. Lastly, the thermometric method (applied to reactions of known kinetic law) allows the effective activation energy to be evaluated from a single experimental curve[11].

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The Differentiating Action of Oxygen-containing Solvents on the Strengths of Acids

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The present review examines the differentiating action of various oxygen-containing solvents on the strength of acids, chiefly carboxylic acids, and nitrophenols. The strength of the acids in these solvents is characterised by the dissociation constants (dielectric constant of solvent > 10) or by the conversion constants (dielectric constant of solvent < 10). The constants were determined by the buffer-free indicator method. The bibliography contains 143 references.

CONTENTS

I. Introduction 818
II. Determination of the strength of acids in solution 819
1. Alcohols and ethers 821
2. Ketones 827
3. Esters 828

I. INTRODUCTION

In the study of electrolytes in non-aqueous solvents, it is often found that the change in their strength is different from that observed in water. This effect of the solvents is called their "differentiating action".

The differentiating action of solvents on the strength of electrolytes, in particular acids, is an important problem in the general theory of solutions. This problem is also of considerable importance in the examination of the reactivities of substances and the mechanisms of reactions in solution. The ability of various non-aqueous solvents to

differentiate the strength of electrolytes is used successfully in chemical analysis. Non-aqueous titration has been finding increasing application in recent years, as indicated by the large number of papers devoted to this topic. These papers have been reviewed by Palit and coworkers[1] and by Kreshkov and coworkers[2-4].

A number of workers have studied the theory of the differentiating action of non-aqueous solvents on the strength of electrolytes. The concept of differentiating and levelling solvents was first introduced by Walden[5,6].

Considerable advances in the theory of electrolyte solutions and in particular the theory of the differentiating action of non-aqueous solvents on the strength of electrolytes have also been made by Soviet workers, particularly Izmailov and coworkers, who have continued the creative development of Mendeleev's ideas on the chemistry of dissolution and who have also introduced the achievements of the physical theory of solutions into the development of general ideas regarding solutions.

Previously, Brönsted[7,8], who studied the strength of acids in non-aqueous solutions, considered that the differentiating action of a solvent depends on its basic strength and dielectric constant. According to his theory, all acids with the same charge, even if of different character, show the same change in strength on going from one solvent to another.

Izmailov[9] showed that the strength of acids with the same charge but of different character (carboxylic acids and nitrophenols) change in different ways on going from water to various non-aqueous solvents. The magnitude of the relative change in the strength of the given acids characterises the differentiating action of the solvents.

According to Izmailov's quantitative theory of the influence of solvents on the strength of electrolytes[10-16], it is necessary, in the examination of the differentiating action of solvents on the strength of acids, to take account of the composition of the products of the reaction of the acid with the solvent, the dielectric constant (DC) and acid–base properties of the solvent, and the solvation of the anions of the acid by solvent molecules.

Hydroxyl-containing solvents may give reaction products with the 1 : 1 composition (with nitrophenols) or the 1 : 2 composition (with carboxylic acids). Solvents which do not contain hydroxyl can give reaction products with the 1 : 1 composition with both types of acid. The difference in the compositions of the products of the reactions of these solvents with acids of different character, compared with those for water, is responsible for their differentiating action. The differentiating action of solvents increases with decrease in the DC and with increase in the acidity of the solvents, and also with change in the energy of solvation of the anions of carboxylic acids.

An extensive review of papers on the differentiating action of non-aqueous solvents on the strength of electrolytes has been made by Izmailov[17,18]. Where necessary, we used material from this review in the examination of the differentiating action of oxygen-containing solvents on the strength of acids.

The present review examines chiefly oxygen-containing solvents of four classes: alcohols, ethers, ketones, and esters; the differentiating properties of acetic anhydride are also examined. The differentiating action of carboxylic acids as solvents was studied in detail by Izmailov and Shkodin[19-23]. They showed that the differentiating action of these solvents on the strength of acids depends chiefly on their DC. This class of solvent will not be examined in the present review.

II. DETERMINATION OF THE STRENGTH OF ACIDS IN SOLUTION

According to Izmailov's theory[10-16], the behaviour of acids in a solvent can be represented as follows:

$$HA + (m+n)M \rightleftarrows HAM_n + {}_mM \rightleftarrows MH_s^+ + A_s^- \rightleftarrows MH_s^+ \cdot A_s^- . \quad (1)$$

The strength of an acid is characterised by the dissociation constant. Electrometric methods, however, measure only the value of K_{form}, which is equal to

$$K_{form} = \frac{[MH_s^+][A_s^-]\gamma^2}{[HA] + [HAM_n] + [MH_s^+ \cdot A_s^-]} . \quad (2)$$

The symbols in Eqn. (2) correspond to scheme (1); γ represents the mean activity coefficient of the ions.

In solvents with high DC, there are almost no associates, so that in these solvents the effective quantity K_{form} and the dissociation constant K_{diss} are equal:

$$K_{form} = K_{diss}\frac{[MH_s^+]^2\gamma^2}{C - [MH^+]\gamma} , \quad (3)$$

where C is the total concentration of acid. In solvents with high DC, electrometric, spectrophotometric, and indicator methods give the same values for the dissociation constants of acids.

In solvents with low DC, however, some of the ions are combined in ion pairs, and these cannot be detected by electrometric measurements. The formation of ion pairs is taken into account in spectrophotometric and indicator methods for determining the strength of acids, where they are regarded as free ions. This explains why in solvents with low DC the values of the dissociation constants of acids and bases determined by electrometric methods are smaller than the values of these constants found by spectrophotometric and indicator methods. This is illustrated in Table 1.

Table 1. pK values for acids in n-butanol.

Acids	pK, electrometric method (Refs.17 and 18)	pK, indicator method (Ref.24)
Acetic	10.35	9.22
Monochloroacetic	8.50	7.31
Dichloroacetic	7.30	6.09
Trichloroacetic	6.30	5.11
Benzoic	10.24	9.18
o-Nitrobenzoic	8.50	7.27
m-Nitrobenzoic	9.15	7.66
p-Nitrobenzoic	9.10	7.74
α-Dinitrophenol*	8.36	6.92
Picric	4.50	3.21

* Presumably 2,6-dinitrophenol, here and subsequently (Ed. of Translation).

The dissociation constants of acids determined by Izmailov using an electrometric method in 50% aqueous acetone are close to the values obtained using the indicator method[25], but in pure acetone[9,25] the two methods give different values. For all acids the dissociation constants determined by the electrometric method are slightly less than the constants obtained by the indicator method (see Table 2). A similar difference was observed by Izmailov and Gurevich[26] in the values of the dissociation constants of picric acid in butanol, found by electrometric and spectrophotometric methods.

In solvents with high dielectric constant, the dissociation constant of an acid is determined by the expression

$$K_{HA} = \frac{[H^+]^2\gamma^2}{(C-[H^+])\,\gamma_{HA}},$$

where γ is the mean activity coefficient of the ions of the acid. γ_{HA}, as the activity coefficient of a non-electrolyte, is close to unity. Since experimental measurements give not $[H^+]$ but $[H^+]\gamma$, and since for most non-aqueous solutions the values of γ are unknown, it is necessary to make the approximation of replacing $[H^+]$ by $[H^+]\gamma$ in the equation for the dissociation constant of the acid. This can be done for dilute solutions, in which γ does not differ greatly from unity. When these approximations are introduced, we obtain for the dissociation constant the expression

$$K_{HA} = \frac{[H^+]^2\gamma^2}{C-[H^+]\gamma}. \quad (4)$$

Table 2.

Acids	50% aqueous acetone		Acetone	
	pK, electrometric method (Ref.17)	pK, indicator method (Ref.25)	pK, electrometric method (Ref.17)	pK, indicator method (Ref.25)
Formic	5.23	5.06	—	9.57
Acetic	6.26	5.86	12.55	10.6
Monochloroacetic	4.28	4.41	9.80	9.21
Dichloroacetic	—	3.17	—	7.70
Trichloroacetic	2.20	2.19	—	6.51
Salicylic	4.18	4.39	9.53	9.08

For a basic indicator in a solution of an acid, we have the equilibrium

$$I_B + H_s^+ \rightleftarrows Ind\,H_s^+. \quad (5)$$

The constant for this equilibrium—the conversion constant of the indicator—is given by the relationship

$$K^I = \frac{[H^+]\gamma\,[I_B]}{[Ind\,H^+]\varkappa} \quad (6)$$

where I_B is the basic form of the indicator, $IndH^+$ the acid form of the indicator, and $\varkappa$ the activity coefficient of the ions of the indicator.

It follows from Eqn. (6) that $[H^+]\gamma = K^I_a$, where $a = \frac{[IndH^+]\varkappa}{[I_B]}$.

We then have

$$K_{HA} = \frac{(K^I a)}{C-K^I a}. \quad (7)$$

The value of K^I can be found[27-29] by solving Eqn. (7) for two acid concentrations C_1 and C_2, at which $a_1 = 1.2$ and $a_2 = 0.8$. It should be noted that the value of C determined colorimetrically is more accurate, the closer it is to unity. When the values of C_1 and C_2 are close to one another, it may be assumed that the mean activity coefficients of the ions of the acid are equal at these concentrations. In this instance we have for K^I the expression

$$K^I = \frac{a_1^3C_2 - a_2^3C_1}{a_1a_2(a_1-a_2)} = \frac{1.44C_2 - 0.64C_1}{0.384}. \quad (8)$$

The determination of K^I is carried out in dilute solutions of strong acids. The calculation of the dissociation constant of a monobasic acid in determinations with an indicator for which K^I has been found is carried out from Eqn.(7) for the acid concentration at which $a = 1$. The following relationship then yields the required constant K_{HA}:

$$K_{HA} = \frac{(K^I)^2}{C-K^I}. \quad (9)$$

If the acid being studied is much weaker than the acid $IndH_s^+$, $[H^+] \ll C$ in the equation for the dissociation constant. In this instance the dissociation constant is calculated using the equation

$$K_{HA} = \frac{(K^I)^2}{C}.$$

Most dissociation constants given by the data of the authors of the present review were obtained for the conditions indicated above. These conditions were achieved by choosing suitable indicators.

To determine the value of K_{HA} in media with low DC, use has been made[30] of the equation

$$K_{HA} = \frac{(K^I)^2 a}{C-K^I a}a^n, \quad (10)$$

where n is a coefficient which takes account of the association of the indicator and acid species. For $a = 1$, $a^n = 1$ for all values of n, so that the value of K_{HA} in this instance is also given by expression (9).

It is better to determine the values of a with a spectrophotometer than with a colorimeter, particularly for a two-colour indicator. When the basic form of the indicator exhibits appreciable absorption at the maximum of the spectroscopic curve of the acid form, it is suggested that a correction be introduced in the calculation[27,28] or that the method of Komar'[31] be used.

The determination of the dissociation constants of bases can be carried out analogously[32].

The method which we proposed for determining the conversion constants of indicators and the dissociation constants of acids and bases was verified for aqueous solutions[27,28]. The agreement in the values found with several acids indicates that the determination of the conversion constant of the indicator in a given solvent is correct. Table 3 gives as examples the values of the conversion constants of indicators obtained with various acids in ethylene glycol.

Several indicators are usually employed to determine reliably the dissociation constant of an acid in a given solvent. The values of pK for the dissociation of a given acid in a given solvent, obtained using different indicators and hence at different concentrations of the acid, differed in our determinations by not more than 0.2 pK unit. This is illustrated in Table 4. The reliability of the determination of dissociation constants by the indicator method which we proposed is also confirmed by the fact that the observed values of the constants differ little from the values measured using the spectrophotometric method (see Table 5).

The buffer-free indicator method for determining the dissociation constants of acids and bases has a number of advantages over other indicator methods. This method makes it possible to determine the dissociation constants of acids and bases and the conversion constants of indicators when none of these quantities are known.

The buffer-free indicator method in non-aqueous solutions should find wider application than the buffer method,

since many salts are sparingly soluble in non-aqueous solvents. Moreover, the ionic strength has a significant influence on the determination in non-aqueous solvents at ionic concentrations at which in water its influence could be neglected. It therefore becomes necessary to take account of the activity coefficients of the ions, but for most non-aqueous solvents these quantities are unknown. An advantage of the indicator method which we have proposed is that with slight approximation it becomes unnecessary to know the activity coefficients of the ions in a given solvent.

Table 3. Determination of the conversion constants of indicators with respect to various acids in ethylene glycol[33].

Acid	Indicator	
	Naphthyl Red	Quinoline Blue
Naphthalene-2-sulphonic	$3.50\cdot10^{-4}$	$2.30\cdot10^{-4}$
Dichloroacetic	$3.20\cdot10^{-4}$	—
Trichloroacetic	$3.80\cdot10^{-4}$	—
Picric	—	$2.43\cdot10^{-4}$

Table 4. Dissociation constants of acids in ethylene glycol[33].

Acids	K_{HA} relative to Quinoline Blue	K_{HA} relative to Naphthyl Orange	K_{HA} relative to Methyl Yellow	Mean K_{HA}	pK	ΔpK
Formic	$(2.42\pm0.38)\cdot10^{-5}$	—	—	$2.4\cdot10^{-5}$	4.62	0.87
Acetic	$(2.50\pm0.17)\cdot10^{-6}$	—	—	$2.5\cdot10^{-6}$	5.60	0.84
Monochloroacetic	$(7.97\pm1.12)\cdot10^{-5}$	$(6.65\pm0.01)\cdot10^{-5}$	—	$7.3\cdot10^{-5}$	4.14	1.27
Dichloroacetic	—	—	$(9.77\pm0.03)\cdot10^{-4}$	$9.8\cdot10^{-5}$	3.01	1.71
Benzoic	$(6.40\pm0.04)\cdot10^{-6}$	—	—	$6.4\cdot10^{-6}$	5.19	0.99
p-Nitrobenzoic	$1.98\cdot10^{-5}$	—	—	$2.0\cdot10^{-5}$	4.70	1.28
m-Nitrobenzoic	$1.85\cdot10^{-5}$	—	—	$1.9\cdot10^{-5}$	4.72	1.28
Salicylic	$(8.47\pm0.9)\cdot10^{-5}$	$(5.50\pm0.66)\cdot10^{-5}$	—	$7.0\cdot10^{-5}$	4.15	1.18
α-Dinitrophenol	$(5.33\pm0.38)\cdot10^{-5}$	—	—	$5.3\cdot10^{-5}$	4.28	0.16
β-Dinitrophenol*	$(5.01\pm0.3)\cdot10^{-5}$	—	—	$5.0\cdot10^{-5}$	4.30	0.53
Boric	$(2.74\pm0.06)\cdot10^{-6}$	—	—	$2.7\cdot10^{-6}$	5.57	−3.69

Note. ΔpK is the difference between the pK values found for the given acid in the solvent used and in water.

* Presumably 3,5-dinitrophenol, here and subsequently (Ed. of Translation).

Table 5. pK values for picric acid.

Alcohol	Spectrophotometric method	Indicator method
t-Butyl[34]	4.43	4.75
n-Hexyl[34]	4.23	4.36
n-Butyl[24]	3.26*	3.21

* Value obtained by Izmailov and Gurevich[26].

It should be noted that the graphical method usually employed to determine the conversion constants of indicators and the dissociation constants of acids or bases is difficult in solvents with low DC, since the regular features of the change in the ratio $[IndH^+]/[Ind]$ with change in acid concentration is complicated by the phenomena of ion association. In solvents with low dielectric constant the strength of acids is characterised by the equilibrium constant for the formation of ion pairs from molecules of the acid:

$$HA \rightleftarrows H_s^+A_s^- . \qquad (11)$$

Following Izmailov, the constant K_{tr} for equilibrium (11) is called the transformation constant (see scheme 1). These equilibrium constants for acids were determined by Kolthoff and Bruckenstein[35], using the indicator method. They examined the following equilibrium between acid and indicator:

$$I_B + HA \rightleftarrows IH_s^+ \cdot A_s^- . \qquad (12)$$

This equilibrium is established in an indifferent solvent, but in a non-indifferent solvent the following equilibrium is energetically more probable:

$$I_B + H_s^+ \cdot A_s^- \leftrightarrows IH_s^+ \cdot A_s^- . \qquad (13)$$

It is evident that the constant for equilibrium (12) depends on the strength of the acid. We proposed a method[29,36] for determining the strength of an acid using the constant for equilibrium (13), that is, the transformation constant of the indicator K_{tr}^I, which is independent of the strength of the acid with which the determination is carried out.

Solvents whose DC are low, but not too low, contain both free ions and ion pairs. For the separate determination of these species, and hence the determination of the constants K_{diss} and K_{tr}, it is necessary to use both electrometric and spectrophotometric or indicator methods. In non-aqueous solvents, particularly those with low DC, the electrometric measurements are often difficult, and comparatively few data are available for these solvents. Difficulties are also encountered in the spectrophotometric determinations, due to the fact that the absorption maxima of the acids or their ions and the solvent are close together, or due to photolysis.

The data obtained by the authors of the present review on the determination of the strength of acids by the indicator method are conditional. Since methods were not available for the separate measurement of the concentrations of free ions and ion pairs, conditional values of the dissociation constants were calculated from the data obtained in solvents with DC > 10, and for solvents with DC < 10 the overall effect was related to the conditional value of the transformation constant of the acid.

1. Alcohols and Ethers

Data on the strength of acids in various alcohols have been obtained by a variety of methods[17,18,37-46]. In an analysis of published data on the strength of acids in methanol, ethanol, and n-butanol, obtained from electrometric measurements, Izmailov[17,18] concluded that alcohols produce a marked decrease in the dissociation constants of all acids, but that the decrease in strength in alcohols compared with water is not quite the same for carboxylic acids and nitrophenols. Izmailov noted that the specific influence of alcohols on the strength of acids is shown more clearly in n-butanol. Thus alcohols differentiate the strength of acids to a slight extent, although they are typical levelling solvents with respect to salts[5,6,47]. The slight increase in the differentiating action of alcohols on the strength of acids in the series methanol (DC = 31.5), ethanol (DC = 24.0), and n-butanol (DC = 17.0) was attributed to the decrease in the DC of the alcohols in this series.

Table 6. pK values for acids in hydroxyl-containing solvents.

Acids	Solvents																
	DC	water [17,18]	n-butanol [24]	n-pentanol [53]	n-hexanol [34]	n-heptanol [53]	n-octanol [53]	n-decanol [53]	isobutyl-alcohol [24]	isopentyl alcohol [48]	t-butyl alcohol [34]	cyclo-hexanol [50]	benzyl alcohol [49]	phenol [52]	ethylene glycol [33]	2-chloro-ethanol [33]	diethylene glycol [51]	diacetone alcohol [51]
			17.1	13.9	13.3	12.0	10.34	—	17.7	15.5	10.9	15.0	13.1	9.78	37,70	25.80	31.7	18.2
	°C	25	20±2	20±2	20±2	20±2	20±2	20±2	20±2	20±2	27±2	27±2	20±2	50±2	20±2	20±2	20±2	20±2
Formic		3.75	8.03	—	7.92	—	—	—	8.85	8.92	8.82	9.02	8.34	5.17	4.62	—	6.64	—
Acetic		4.75	9.22	—	9.26	—	—	—	10.35	10.51	10.30	10.68	9.71	6.58	5.60	7.72	7.35	—
Monochloroacetic		2.86	7.31	7.85	7.24	6.35	—	—	8.11	8.48	8.51	8.60	7.88	4.85	4.14	5.55	5.82	—
Dichloroacetic		1.30	6.09	6.46	6.29	5.76	7.48	3.34*	6.85	7.07	7.20	7.19	6.43	—	3.01	—	4.38	7.60
Trichloroacetic		0.70	5.11	5.47	5.51	4.88	6.53	2.62*	5.62	5.32	6.82	6.04	5.37	—	—	—	2.82	6.39
Benzoic		4.20	9.18	9.53	9.11	8.40	—	—	10.20	10.92	9.80	11.34	9.62	6.80	5.19	7.68	6.96	—
o-Nitrobenzoic		2.17	7.27	8.17	7.22	6.90	8.77	—	8.37	—	8.57	8.70	—	4.75	—	—	—	—
m-Nitrobenzoic		3.49	7.66	8.53	7.85	7.16	9.77	—	—	9.17	9.20	9.40	8.60	6.15	4.72	6.43	5.64	—
p-Nitrobenzoic		3.40	7.74	—	7.52	—	—	—	8.78	9.07	9.44	9.58	8.38	5.70	4.70	6.49	6.24	—
Salicylic		2.97	7.51	8.14	7.48	6.71	9.33	—	8.25	8.50	8.66	8.78	8.40	5.30	4.15	5.42	5.82	—
α-Dinitrophenol		4.02	6.92	7.49	6.89	6.11	8.74	—	7.54	7.89	7.30	7.58	8.34	7.04	4.28	6.15	5.48	8.43
β-Dinitrophenol		3.80	6.92	7.24	6.85	5.90	8.23	—	7.54	7.82	6.89	8.10	8.38	6.62	4.28	6.25	5.48	8.43
Picric		0.80	3.21	3.92	4.36	3.70	4.29	1.21*	3.96	4.30	4.70	3.57	4.42	—	—	—	3.12	—
Boric		9.24**	—	—	—	—	—	—	—	—	—	—	—	—	5.57	—	—	—

* pK_{tr}. ** pK_1.

Table 7. $\Delta pK = pK_{\text{in alcohol}} - pK_{\text{in water}}$.

Acids	Solvents														
	n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol	isobutyl alcohol	isopentyl alcohol	t-butyl-alcohol	cyclo-hexanol	benzyl alcohol	phenol	ethylene glycol	2-chloro-ethanol	diethylene glycol	diacetone alcohol
Formic	4.28	—	4.17	—	5.83	5.10	5.17	5.07	5.27	4.59	1.42	0.87	—	2.89	—
Acetic	4.47	—	4.50	—	—	5.59	5.75	—	5.92	4.95	1.82	0.84	2.96	2.59	—
Monochloroacetic	4.45	4.98	4.37	3.49	—	5.24	5.61	5.64	5.73	5.01	2.00	1.27	2.68	2.95	—
Dichloroacetic	4.79	5.16	4.99	4.46	6.18	5.55	5.77	5.90	5.98	5.13	—	1.71	—	3.08	6.30
Trichloroacetic	4.41	4.77	4.81	4.18	5.83	4.92	4.62	6.12	5.34	4.67	—	—	—	2.12	5.69
Benzoic	4.98	5.33	4.91	4.20	—	6.00	6.72	5.60	7.14	5.42	2.60	0.99	3.48	2.76	—
o-Nitrobenzoic	5.10	5.97	5.02	4.73	6.60	6.20	—	6.37	6.50	—	2.20	—	—	—	—
m-Nitrobenzoic	4.17	5.06	4.36	4.67	6.28	—	5.68	5.71	5.91	5.11	2.68	1.28	2.96	2.15	—
p-Nitrobenzoic	4.32	—	4.12	—	—	5.38	5.67	6.04	6.17	4.96	2.30	1.28	3.07	2.84	—
Salicylic	4.54	5.17	4.51	3.74	6.36	5.28	5.53	5.69	5.80	5.12	2.32	1.18	2.45	2.85	—
α-Dinitrophenol	2.90	3.47	2.87	2.09	4.72	3.52	3.87	3.28	3.55	4.32	2.94	0.16	2.13	1.46	4.41
β-Dinitrophenol	3.12	3.44	3.05	2.10	4.43	3.74	4.02	3.09	4.30	4.58	2.85	0.53	2.41	1.68	4.63
Picric	2.41	3.12	3.56	2.90	3.49	3.16	3.50	3.90	2.77	3.62	—	—	—	—	—
Boric	—	—	—	—	—	—	—	—	—	—	—	3.67	—	—	—

We used the buffer-free indicator method to study the strengths of a series of acids of different character in various primary, iso-, secondary, and tertiary alcohols, and also in alcohols with two functional groups: ethylene glycol, 2-chloroethanol, diethylene glycol, and diacetone alcohol [24,33,34,48-53]. In alcohols with intermediate DC values, the dissociation constants of the acids were calculated, and in alcohols with DC less than 10, the transformation constants were calculated. The results are given in Table 6, which also gives the pK values for the acids in water [17,18]. The decrease in the strengths of carboxylic acids in alcohols relative to their strengths in water is different for different acids; the strengths of nitrophenols change to a smaller extent.

The change in the strength of acids on going from water to a non-aqueous solvent is characterised by the quantity $\Delta pK = pK_{\text{in alcohol}} - pK_{\text{in water}}$. The greater the quantity ΔpK, the greater the decrease in the strength of acids in the given solvent compared with water. The values of ΔpK obtained for the alcohols studied are given in Table 7. The decrease in the strength of *o*-nitrobenzoic acid on going from water to alcohols is greater than the decrease in strength shown by all other carboxylic acids. This phenomenon can be explained on the basis of the steric effects arising in the reaction of the molecules and ions of this acid with the solvent. In the *o*-nitrobenzoic acid molecule, an intramolecular hydrogen bond may be formed between the NO_2 and COOH groups, and this is broken on interaction with the solvent. Thus the reaction of the molecules of this acid with the solvent depends on steric effects to a greater extent than the reaction of other carboxylic acids whose molecules do not contain an intramolecular hydrogen bond. For salicylic acid, whose molecule contains a hydroxyl group in the *ortho*-position, an effect similar to that observed for *o*-nitrobenzoic acid should have been found. However, the decrease in the strength of this acid on going from water to alcohols was found to be approximately the same as that for other carboxylic acids. As noted above, the strength of an acid depends on the reaction of the acid with the solvent and on the subsequent solvation of the ions formed. Thus the observed contradictions are apparently explained by the suggestion [54-57] that the salicylate ion formed on ionisation of the acid contains an intramolecular hydrogen bond and is stable.

The decrease in the strength of nitrophenols on going from water to alcohols with two functional groups is slightly smaller than that observed for carboxylic acids, but the

decrease in strengths is almost the same in diethylene glycol.

It is convenient to estimate the differentiating action of solvents from graphs giving the dependence of pK for the acids in alcohol on their pK values in water. As already noted[17], different straight lines are obtained graphically for acids of different character (carboxylic acids and nitrophenols) in differentiating solvents. For some acids, particularly *o*-nitrobenzoic acid, the pK values do not lie directly on the straight line for carboxylic acids, because of the specific interaction of the acid with the solvent. The differentiating properties of a given solvent can be estimated from the distance between the straight lines on the graph of the dependence of pK for the acids in the non-aqueous solvent on the pK values for the acids in water. This distance (Δ'pK), expressed in pK units, gives the difference between the change in the strength for acids of different chemical character on going from water to the non-aqueous solvent expressed in orders of magnitude. The Δ'pK values obtained from data on the strength of acids in alcohols (Table 6) are given in Table 8.

Table 8. Differentiating action of alcohols.

Alcohols	DC	Δ'pK (from graphs)	Alcohols	DC	Δ'pK (from graphs)
Benzyl	13.1	1.0	Isopentyl	15.5	1.9
n-Butyl	17.1	1.8	t-Butyl	10.9	2.4
n-Pentyl	13.9	1.9	Phenol	10	−0.8*
n-Hexyl	13.3	1.5	Cyclohexanol	15.0	2.5
n-Heptyl	12.0	1.7	Ethylene glycol	37.70	≈1.0
n-Octyl	10.34	2.0	Diethylene glycol	31.69	1.1
n-Decyl	<10	1.6*	2-Chloroethanol	25.8	0.8
t-Butyl	17.7	1.9	Diacetone	18.2	1.6*

* Estimated approximately from the data in Table 6.

On going from n-butanol to n-octanol in the series of normal alcohols, the differentiating properties change little, although the DC values of the alcohols decrease. Thus the differentiating properties of these alcohols cannot be attributed to the influence of their DC.

The differentiating properties of alcohols are influenced by their acid–base properties. The acidity of simple aliphatic alcohols decreases with increase in the electron-donating properties of the alkyl group[58]. Work by Gerrard and Macklen[59-61] on the solubility of hydrogen chloride in alcohols showed, however, that n-butanol, n-hexanol, n-heptanol, and n-octanol have almost identical electron-donating properties. Thus for the example of these normal alcohols it is possible to follow the influence of one predominant factor—the increase in the length of the alkyl radical of the alcohol—on the differentiating properties of the alcohol.

It can be seen from the results obtained that the increase in the length of the alcohol radical from butanol to decanol has little influence on the differentiating properties of the alcohol, since the increase in the radical of the primary alcohol hardly affects the screening of the functional group of the alcohol and does not produce any significant steric effects in the reaction of the molecules of these solvents with carboxylic acid dimers.

Comparison of the differentiating properties of the normal alcohols and iso-alcohols leads to the conclusion that branching of the radical in the alcohol molecule at a carbon atom which is not joined to a hydroxyl group produces little change in the differentiating properties of the alcohols.

Of the alcohols with one functional group which we studied, benzyl alcohol shows the weakest differentiating properties. The DC of this alcohol is almost the same as that of n-hexanol. The weak differentiating properties of benzyl alcohol can probably be attributed to the fact that it exhibits stronger acidic properties than the other normal alcohols, and its radical has little steric effect on the reaction of two molecules of the alcohol with a molecule of the carboxylic acid. Thus carboxylic acids are stronger acids in benzyl alcohol than in other alcohols.

The more acidic solvent, phenol, with a planar radical, produces a change in the relative strength of acids which is the opposite of that observed for alcohols, in spite of the fact that phenol has a low DC. The decrease in the strength of carboxylic acids in phenol is less than that shown by nitrophenols.

The secondary alcohol cyclohexanol is a differentiating solvent, although its DC is of the same order of magnitude as the DC of normal alcohols, iso-alcohols, and benzyl alcohol. It is also a more basic solvent than the alcohols already considered. Thus the marked differentiating action of this alcohol on the strength of acids is apparently related to the spatial complexity of its radical.

t-Butyl alcohol is also a strongly differentiating solvent.

It may be concluded that the differentiating properties of secondary and tertiary alcohols are related to the spatial complexity of the radicals of these alcohols close to their functional groups; this creates considerable steric hindrance in the reaction of the molecules of these alcohols with carboxylic acid dimers.

Of the alcohols studied, ethylene glycol has the highest DC, so that it should exhibit weaker differentiating properties than the other alcohols. The data obtained, however, indicate that ethylene glycol is a slightly stronger differentiating solvent than benzyl alcohol and 2-chloroethanol—solvents with smaller DC.

Published data[58-70] show that all the alcohols studied differ little in acid–base properties, with the exception of ethylene glycol and 2-chloroethanol.

2-Chloroethanol is the most strongly acidic of the alcohols studied, so that despite the fact that its radical is more complex than the radical of benzyl alcohol, it exhibits weaker differentiating properties.

Although ethylene glycol has a high DC and is a more acidic solvent than benzyl alcohol, its differentiating action on the strength of acids is approximately the same, so that its radical produces greater steric hindrance in the reaction with carboxylic acid dimers than benzyl alcohol. The strength of boric acid has been determined in ethylene glycol; boric acid reacts with this solvent to form a complex which behaves as a monobasic acid[71].

Diethylene glycol is $\beta\beta'$-dihydroxydiethyl ether. The presence of the ether group explains why it is a stronger base than ethylene glycol. The oxygen of this ether group can react with acids. This atom is screened to a greater extent, however, than the oxygen of the hydroxyl group, so that the differentiating properties of diethylene glycol are stronger than those of ethylene glycol.

From its DC, the differentiating properties of diacetone alcohol should be the same as those of isobutyl alcohol, but on the basis of the structure of its radical it should exhibit stronger differentiating properties than all other alcohols. According to the studies of Badger and Bauer[72,73], diacetone alcohol contains an intramolecular hydrogen bond. These authors also compare the structure of this alcohol

with that of t-pentyl alcohol. Thus the molecule of this alcohol should create greater steric hindrance in its reactions not only with carboxylic acids but also with nitrophenols. As a result, the change in the relative strength of acids of different character is approximately the same in this solvent as in isobutyl alcohol.

As noted above, one of the factors influencing the differentiating properties of solvents is the difference in the solvation of the anions of acids of different character by these solvents. Izmailov and coworkers[74-78] showed that on going from water to levelling solvents the change in the solvation energy of the molecules becomes greater than the change in the solvation energy of the ions; in differentiating solvents, however, the opposite relationship is observed. Thus in the examination of the differentiating properties of solvents it is necessary to take into account the reaction of both the ions and the molecules of the acid with the molecules of the solvent.

To obtain information on the relative change in the energy of solvation of the anions of carboxylic acids and nitrophenols in the alcohols studied, we determined the heats of dissolution of the diethylammonium salts of carboxylic acids and nitrophenols[79-81]. The heats of solvation of the ions in different solvents are fairly close, but, as shown by Izmailov[82], even slight differences in the values lead to a marked change in the strength of the acid.

Table 9. Heats of dissolution ΔH, kcal mole^{-1}, of diethylammonium salts in alcohols and cyclohexane[79-81].

Diethylammonium salt	Water (27°C)	Water (41°C)	2-Chloroethanol (27°C)	Benzyl alcohol (27°C)	Ethylene glycol (27°C)	Diethylene glycol (27°C)	Cyclohexanol (41°C)	t-Butyl alcohol (27°C)	Cyclohexanol (27°C)
Chloride	0.3	2.6	—2.0	0.7	2.1	2.1	4.0	—	0.2
Bromide	1.8	3.8	0.7	1.9	3.5	2.0	2.4	—	5.6
Trichloroacetate	1.8	5.3	1.7	2.2	3.6	3.0	8.6	7.5	5.6
Salicylate	2.8	5.9	—0.8	2.6	3.8	1.4	5.2	4.5	4.5
Benzoate	*	0.8	—1.4	2.2	2.9	*	4.6	8.1	5.2
Acetate	—0.8	—4.9	1.1	2.7	3.6	3.3	—	—	8.7
α-Dinitrophenolate	—4.1	10.5	2.9	4.4	5.4	—	10.9	—	5.7
β-Dinitrophenolate	4.6	8.7	3.5	4.9	6.0	—	8.2	—	5.4
Picrate	4.7	8.0	3.0	2.9	5.1	*	7.7	9.1	3.5

* Sparingly soluble salt.

In the analysis of the data in Table 9 it is necessary to take into account the familiar ideas of physical chemistry, according to which an increase in the exothermicity of the dissolution of a given salt in different solvents is due to an increase in the energy of solvation of its ions.

The data in Table 9 indicate that the relative exothermic nature of the solvation of the anions of acids increases in the order: t-butyl alcohol, ethylene glycol, diethylene glycol, benzyl alcohol, 2-chloroethanol. The most strongly exothermic process is the solvation of the salts in 2-chloroethanol, and this is evidently related to the fact that the acidic properties of this alcohol are stronger than those of the other alcohols. With increase in the acidity of the alcohol, the hydrogen bond which it forms with the ions of the acids studied disappears.

It can be seen from the heats of dissolution of the salts (Table 9) that the exothermic nature of the solvation of the anions of the acids decreases considerably on going from water to cyclohexanol (with the exception of salicylate). For the salts formed by nitrophenols, the changes in the heats of solvation are not large. Thus the differentiating properties of cyclohexanol are related to the fact that the heats of solvation of the anions of carboxylic acids are smaller in cyclohexanol than in water.

The heats of solvation of the salicylate ion in different alcohols are approximately the same (judging from the heats of dissolution of diethylammonium salicylate, given in Table 9). This can be attributed to the fact that the salicylate ion contains an intramolecular hydrogen bond, so that it reacts weakly with the OH group of the solvent and the spatial complexity of the radical of the solvent has no significant influence on the heat of solvation of this ion.

As already noted, in the examination of the differentiating properties of solvents it is necessary to take into account the reaction of not only the ions but also the molecules of the acid with the molecules of the solvent. Izmailov showed that the energy of solvation of the molecules of acids depends on the strength of the complex formed between the acid and the solvent. If the solvent is more basic, the energy of solvation of the molecules will be greater, and the solvation will become more exothermic. On the basis of the data which we obtained[79] (Table 10) it may be concluded that the change in the integral heats of dissolution of benzoic and salicylic acids and α-dinitrophenol on going from the levelling solvent benzyl alcohol to the differentiating solvent cyclohexanone (a ketone) is not large. The energy of the reaction of the molecules of the acids with cyclohexanone is greater than that for benzyl alcohol, since cyclohexanone is a slightly more basic solvent than benzyl alcohol.

Table 10. Integral heats of dissolution of acids[79] (27°C).

Acids	ΔH, kcal mole^{-1}	
	cyclohexanone	benzyl alcohol
Benzoic	3.5	4.7
Salicylic	2.1	3.8
α-Dinitrophenol	3.9	5.3

It may therefore be concluded that the differences in the differentiating properties of alcohols are related chiefly to differences in the energies and heats of solvation of the anions of carboxylic acids compared with the anions formed by nitrophenols. The increase in the differentiating action of the solvents is related to the decrease in the exothermic nature of the solvation of the ions of the carboxylic acids. The exothermic nature of the solvation of the anions of carboxylic acids in turn decreases with increase in the spatial complexity of the radicals of the alcohols.

It follows from the foregoing that the differentiating action of alcohols on the strength of acids is due to a number of factors: the spatial complexity of the radicals of the solvent, the difference in the solvation of the anions of acids of different character (this also depends on the spatial complexity of the solvent molecules), and the acidity of the solvent. Both levelling and differentiating solvents can be found among alcohols, depending on the combination of these factors.

Like alcohols, ethers contain an alkoxy-oxygen, which is screened by two radicals. Thus the reaction of ethers

with acids should be influenced considerably by steric factors associated with the screening of the functional group of the ether by the radicals. This is indicated by published data[83-86] on the basis of which we should expect that the differentiating properties of ethers will also depend to a marked extent on the nature and spatial complexity of their radicals.

We studied the strength of various carboxylic acids and nitrophenols in various ethers: diphenyl (diphenyl oxide), methyl phenyl (anisole), diethyl, dibenzyl, di-(2-chloroethyl) (Chlorex), dibutyl, and di-isopentyl[36,87,88]. All these ethers, with the exception of Chlorex, have low dielectric constants (in the range 2–5), so that the strength of acids in these solvents should be characterised by the transformation constants, which we determined by the proposed method. The transformation constants of picric acid were first determined spectrophotometrically. We recorded the spectra of solutions of picric acid in the ethers and with the addition of a strong base in the range 370–470 nm. The spectra of solutions of picric acid in a given ether with the addition of an excess of diethylamine or piperidine coincided. The spectroscopic curves for the picrate solutions show a slight maximum in the range 400–420 nm, characteristic of the associated ions of picric acid[89]. We calculated the values of the transformation constants for picric acid in ethers from the absorption at various wavelengths in the spectral range studied. It was found that the calculated values of the constants remained almost constant in the wavelength range 440–480 nm. With decrease in wavelength, however, the values of the constants gradually increased. This is apparently due to the fact that in this range, absorption by molecules of the acid increases gradually towards shorter wavelengths, and this was not taken into account in the calculation. Table 11 therefore gives the mean values of pK_{tr} for picric acid, calculated for the wavelength range 440–480 nm. The calculation of the transformation constants of picric acid was based on the assumption that the ionic associates obtained by the reaction of picric acid with strong bases (diethylamine or piperidine) and with ethers acting as bases have the same absorption spectra in the range used for the calculations; molecules of picric acid do not absorb in this range. Justification for this assumption is provided by the agreement observed in the dissociation constants of picric acid in alcohols, determined by spectrophotometric and indicator methods. The spectrophotometric determination of the dissociation constants of this acid was based on the same assumptions as the determination of its transformation constants in the ethers. The transformation constants of the indicators were then determined with respect to picric acid, and the values were used to determine the transformation constants of carboxylic acids and dinitrophenols.

Examination of the pK_{tr} values for the acids in the ethers studied (Table 11) shows that the strengths of nitrophenols in the ethers studied do not differ greatly. The strengths of carboxylic acids in ethers with different radicals, however, differ sharply and a correlation is not observed between the basic strength of the ethers and the strengths of carboxylic acids in these ethers.

According to published data[61,90-95], the ethers studied can be arranged in the following order of increasing basic strength: diphenyl oxide < anisole < Chlorex < dibenzyl ether < diethyl ether < dibutyl ether.

In diphenyl oxide—the ether with the lowest basic strength—the carboxylic acids are much weaker than in the more basic diethyl ether, and the value of K_{tr} for trichloroacetic acid is smaller by almost three orders of magnitude in dibutyl ether than in diphenyl oxide. The strength of the carboxylic acids decreases with increase in the spatial complexity of the radicals of the ether (Table 11). The differentiating action of ethers is characterised by the values of $\Delta' pK_{tr}$, found from graphs giving the dependence of the values of pK_{tr} in the corresponding ether on the pK values in water (Table 12).

Table 11. pK_{tr} values for acids in ethers[36,87,88].

Acids		Solvents					
		dibutyl ether	diethyl ether	benzyl ether	anisole	diphenyl oxide	Chlorex
	DC	3.06	4.34	5.1	4.33	2.35	21.20
	°C	20±2	20±2	20±2	20±2	30±2	20±2
Formic		—	—	5.05	4.74	4.04	—
Acetic		—	—	—	4.85	5.48	—
Monochloroacetic		—	5.85	4.54	3.97	3.05	—
Dichloroacetic		—	4.52	2.54	2.00	1.82	7.47*
Trichloroacetic		3.07	2.52	2.26	1.00	0.35	6.62*
Benzoic		—	—	—	5.71	5.23	—
Salicylic		—	5.76	—	4.05	3.41	—
o-Nitrobenzoic		—	5.12	—	3.67	2.65	—
m-Nitrobenzoic		—	—	—	4.42	3.65	—
p-Nitrobenzoic		—	—	—	4.62	4.08	—
α-Dinitrophenol		—	4.87	—	4.24	5.00	—
β-Dinitrophenol		—	4.23	5.20	4.38	4.14	—
Picric		1.09	1.52	2.00	1.05	1.57	5.52*

* pK.

Table 12.

Ethers	$\Delta' pK_{tr}$
Diphenyl oxide	0
Anisole	0.3
Dibenzyl	0.2
Diethyl	1.5
Dibutyl	2.0
Chlorex	1.2*

* $\Delta' pK$.

Examination of the results obtained shows that diphenyl oxide is a levelling solvent and that in this solvent we even observe a slight relative decrease in the strength of nitrophenols compared with carboxylic acids. We observed a similar but more clearly defined influence on the strength of acids in phenol. Anisole and dibenzyl ether show a very slight differentiating action, whereas ethers with saturated radicals are strongly differentiating solvents, and this property becomes more marked with increase in the size of the radicals. Diethylammonium and piperidinium picrates are insoluble in isopentyl ether, so that only the concentrations of picric and trichloroacetic acids at which half of the indicator Naphthyl Red is converted into the acid form were determined. These data[88] show that the differentiating properties of di-isopentyl ether are similar to those of dibutyl ether, that is, di-isopentyl ether is a strongly differentiating solvent. For Chlorex, $\Delta' pK$ = 1.2, and this characterises it as a differentiating solvent, although its differentiating properties are weaker than those of the other ethers having saturated radicals studied.

Ethers are solvents which cannot act as proton donors, so that it might be expected that they would all be differentiating solvents. The observed variation between their differentiating properties, which depend on the structure of the radicals in the ether molecule, indicates that steric factors have a marked influence on the reaction of the carboxylic acid dimers with the molecules of the ether.

To investigate the factors influencing the differentiating properties of ethers, we studied the heats of dissolution of benzoic acid and two dinitrophenols, and also diethylammonium β-dinitrophenolate, benzoate, and trichloroacetate in anisole, Chlorex, and dibutyl ether. The results[88] indicate that the relative change in the heats of dissolution of the acids and their salts on going from a levelling ether to a differentiating ether is not large, and its nature is such that it cannot explain the variation in the differentiating properties of ethers.

Information on the mechanism of the reaction of carboxylic acids with alcohols can be obtained from the infrared spectra of solutions of these acids in the alcohols.

Izmailov and coworkers[89,96,97] previously studied the reaction of carboxylic acids with alcohols from the Raman spectra in the range of the ν_{max} band of the C=O group. Only the reaction of carboxylic acids with weakly differentiating alcohols was studied.

Carboxylic acids exist in the form of dimers. The monomeric form of the acid is produced in solution as a result of the reaction of the acid dimers with solvent molecules. In the acid dimer, the hydrogen bond between the hydroxyl group of the acid and the carbonyl oxygen is stronger than that between this oxygen and the hydroxyl group of the alcohol which reacts with the acid, because the hydroxyl group of the acid has a greater tendency to give up a proton than the hydroxyl group of the alcohol. Thus breakdown of the dimer should take place as a result of the reaction of the oxygen of the hydroxyl group of the alcohol with the hydrogen of the hydroxyl group of the acid. To determine how carboxylic acids react with levelling and differentiating alcohols, we studied the infrared spectra of trichloroacetic acid in various alcohols, examining the region of the stretching vibrations of the C=O and OH (OD) groups of the acid[98].

No significant displacement of the main ν_{max} band due to the C=O group was observed on going from one alcohol to another. This indicates that the alcohols which we studied influence the position of the band due to the carbonyl group of the acid in the same way.

We assigned the main intense band (~ 1750 cm^{-1}) to the vibrations of the C=O group of the acid monomers, since it may be assumed that the carboxylic acid dimers are broken down in solvents capable of forming a strong hydrogen bond with the acid molecule. In this connection it may be noted that according to data obtained by Izmailov and coworkers[89,97] and ourselves[98], the νC=O band of the acid dimers in the infrared and Raman spectra was observed only in fairly concentrated solutions of acetic acid in alcohols.

In the infrared spectra of solutions of trichloroacetic acid in strongly differentiating solvents (cyclohexanol and t-butyl alcohol) we observed a weak band in the range 1700–1715 cm^{-1}, which may be assigned to the vibrations of the C=O group of the acid dimer. On dilution, the intensity of this band decreased, and the intensity of the band due to the C=O group of the acid monomers increased. In the spectra of solutions of trichloroacetic acid in weakly differentiating alcohols, we did not observe the band due to the C=O group of the acid dimers. It can evidently be assumed that the given solvents react more strongly with trichloroacetic acid than do differentiating solvents. Thus the quantity of dimers in these solvents is not large and has no influence on the stretching vibrational band of the carbonyl group of the acid. This also agrees with the fact that trichloroacetic acid is a weaker acid in strongly differentiating alcohols than in levelling alcohols.

Thus the data obtained indicate that the probability of reaction of carboxylic acids with strongly differentiating alcohols is less than that for levelling alcohols. This can be related to the steric effects which must be taken into account in the reaction of carboxylic acids with differentiating solvents.

We studied the infrared spectra of CCl_3COOH and CCl_3COOD in anisole and dibutyl ether[98]. These data give information on the reaction of the carboxylic acid with solvents containing alkoxy-oxygen. Study of the spectra indicated that the hydrogen bond formed by ethers with the hydroxyl group of the acid is stronger than that formed by alcohols. The νOH bands for the acid monomers in ethers lie in the range 2800–3100 cm^{-1}. The corresponding νOD bands in ethers should be displaced towards lower frequencies[99,100]; they appear at 2180 cm^{-1} in dibutyl ether and at 2270 cm^{-1} in anisole. It can be seen from these data that the hydrogen bond formed by trichloroacetic acid with dibutyl ether is stronger than that formed with anisole. This agrees with the fact that dibutyl ether is a more basic solvent, that is, it has a stronger electron-donating power than anisole.

The bands observed in the range 2550–2600 cm^{-1} in the spectra of CCl_3COOH were assigned to the vibrations of the OH group of the acid dimers. In the spectra of CCl_3COOD in ethers the corresponding bands due to the vibrations of the OD bonds of the acid dimers lie in the range 2030–2060 cm^{-1}.

The frequency of the stretching vibrations of the C=O group of the acid in ethers at 1765–1770 cm^{-1} is slightly greater than that of the band in alcohols (1750 cm^{-1}); this can be attributed to the absence of the perturbing influence of the hydrogen bond on the carbonyl group.

Ginzburg and Abramovich[101], in a study of the reaction of trichloroacetic acid with ethers, showed that in equimolar mixtures of the acid and ethers in CCl_4 the absorption band of the carbonyl group of the acid dimers appears in the form of a shoulder. In our studies, carried out in ethers without an inert solvent, there was almost no trace of a band due to the acid dimers in this range. The presence of bands characteristic of hydrogen bonds formed by the OH (OD) group of the acid, however, indicates that the solutions studied contain some acid dimers. The relative concentration of dimers is greater in dibutyl ether than in anisole, that is, the probability of reaction of the acid with dibutyl ether is less than that for anisole, although the hydrogen bond formed by the trichloroacetic acid molecules with dibutyl ether is stronger than that formed with anisole. This agrees with the data obtained by Ginzburg and Abramovich[101], according to which dibutyl ether, in its reaction with trichloroacetic acid, appears to exhibit weaker electron-donating properties than propyl and ethyl isobutyl ethers. It may therefore be concluded that the relative decrease in the strength of trichloroacetic acid in dibutyl ether compared with anisole is due not so much to the strength of the hydrogen bond between the acid and the ether as to the probability of its formation.

We also recorded the infrared spectra of diethylammonium trichloroacetate in the alcohols studied[98]. No significant displacement of the band due to the asymmetric stretching vibrations of the carboxylate ion (1680 cm^{-1}) in different alcohols was observed. The difference in the

reactions of the trichloroacetate ion with alcohols apparently does not influence the frequency of the asymmetric stretching vibrations of the carboxylate ion.

2. Ketones

The strengths of many acids in acetone and aqueous acetone mixtures were studied by Izmailov and coworkers[9], using electrometric methods. They showed[102,103] that the differentiating action of acetone is due to the formation of a reaction product with 1 : 1 composition by the carboxylic acids and the ketone, in contrast to the product with the 1 : 2 composition obtained in water and alcohols[96,103,104].

The authors cited also showed that the differentiating action of acetone on the strength of acids is related to a decrease in the solvation energies of the anions of the carboxylic acids compared with their solvation energies in water. The solvation energies of the anions formed by nitrophenols in acetone differ comparatively little from their energies of solvation in water[105,106].

We used the buffer-free indicator method to study the strength of acids in various ketones, including acetone[25,107,108]. The pK values for acids in these solvents, and the values of ΔpK and Δ'pK, are given in Tables 13, 14, and 15 respectively.

Table 13. pK values for acids in ketones[25,107,108] and acetic anhydride[109].

Acids		Solvents				
		acetone	acetophenone	benzophenone	cyclohexanone	acetic anhydride
	DC	20.7	17.39	13.3	18.3	20.7
	°C	20±2	20±2	53±2	22±2	22±2
Formic		9.57	8.61	—	8.83	—
Monochloroacetic		9.21	8.31	—	8.16	8.73
Acetic		10.62	10.03	—	—	—
Dichloroacetic		7.70	7.41	7.96	6.85	7.84
Trichloroacetic		6.51	6.26	6.14	5.66	6.78
Propionic		—	10.07	—	—	—
Benzoic		—	9.80	—	—	—
Salicylic		9.08	8.14	—	8.01	—
o-Nitrobenzoic		—	8.14	—	8.23	—
m-Nitrobenzoic		—	8.62	—	8.68	—
p-Nitrobenzoic		—	8.72	—	8.70	—
α-Dinitrophenol		7.55	7.36	—	7.32	—
β-Dinitrophenol		7.77	7.47	—	7.33	—
Picric		4.14	4.55	5.29	4.24	5.97

The results (Tables 13–15) show that all the ketones which we studied are differentiating solvents. The basic strengths of the ketones studied are similar[90,110–112], but if we nevertheless arrange them in order of increasing basic strength—benzophenone < acetophenone < acetone < cyclohexanone—and compare the order with the order of the pK values for picric acid in the same solvents, we may conclude that the strength of picric acid increases in accordance with the increase in the basic properties of the ketone. The strengths of carboxylic acids in all the ketones decrease considerably compared with the values for water, and the decrease is much greater than that for nitrophenols.

The ketones which we studied exhibit similar differentiating properties, but when the methyl radicals in the acetone molecule are replaced by phenyl radicals (Table 15), the differentiating properties of the corresponding ketones decrease. Although the effect is weak, ketones apparently show steric effects in the reaction of the carboxylic acid dimers with the solvent. The fact that the influence of the radicals of the ketones on the differentiating properties of these solvents is slight can be attributed to the fact that the radicals in ketones are further removed from the oxygen than in alcohols and ethers.

Table 14. ΔpK values for acids.

Acids	Solvents				
	acetone	acetophenone	benzophenone	cyclohexanone	acetic anhydride
Formic	5.82	4.89	—	5.08	—
Acetic	5.86	5.27	—	—	—
Monochloroacetic	6.34	5.43	—	5.29	5.86
Dichloroacetic	6.40	6.11	6.66	5.55	6.54
Trichloroacetic	5.81	5.56	5.44	4.96	6.08
Propionic	—	5.20	—	—	—
Benzoic	—	5.60	—	—	—
Salicylic	6.11	5.17	—	5.01	—
o-Nitrobenzoic	—	5.98	—	6.07	—
m-Nitrobenzoic	—	5.13	—	5.19	—
p-Nitrobenzoic	—	5.32	—	5.30	—
α-Dinitrophenol	3.53	3.34	—	3.30	—
β-Dinitrophenol	3.97	3.68	—	3.53	—
Picric	3.64	3.75	4.49	3.44	5.17

To investigate the influence of differences in the solvation of the anions of acids of different character on the differentiating properties of ketones, we studied the heats of dissolution of diethylammonium salts in cyclohexanone. The results (Table 9) show that in cyclohexanone, as in acetone, there is a relatively greater decrease in the solvation energy of the anions of carboxylic acids, compared with the anions of nitrophenols, on going from water to the ketone.

Table 15. Differentiating action of ketones and acetic anhydride.

Solvent	Δ'pK
Acetone	2.5
Acetophenone	1.7
Benzophenone	1.3
Cyclohexanone	1.6
Acetic anhydride	1.1

All the ketones studied are differentiating solvents and can be used in non-aqueous titration.

Tables 13–15 also give data on the strength of acids in acetic anhydride[109] and its differentiating properties. The data show that acetic anhydride is a differentiating solvent, although its differentiating action is weaker than that of ketones. Because of the acidic properties of acetic anhydride, acids dissolved in this solvent are slightly weaker than in ketones.

Table 16. Values of pK_{tr} and pK_{diss} for acids in esters.

Acids		Solvents												
		water	butyl acetate (Ref.120)	ethyl acetate (Ref.118)	benzyl acetate (Ref.118)	phenyl acetate (Ref.119)	ethyl monochloroacetate (Ref.119)	acetoacetic ester (Ref.119)	diethyl carbonate (Ref.119)	ethylbenzoate (Ref.118)	Acetone-benzene (Ref.119)	tributyl phosphate (Refs.119,120)	triphenyl phosphate (Ref.120)	tricresyl phosphate (Ref.121)
	DC	81.0	5.01	6.02	5.10	5.38	20	15.7	2.82	6.06	6.02	7.97	—	6.7
	°C	25	20±2	22±2	22±2	22±2	22±2	22±2	22±2	22±2	22±2	20±2	49±2	20±2
		pK_{diss}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{diss}	pK_{diss}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}	pK_{tr}
Trichloroacetic		0.70	1.14	1.60	2.57	1.51	6.57	6.28	2.52	1.92	1.55	3.32	2.69	—
Dichloroacetic		1.30	3.86	3.08	3.75	3.06	—	7.48	4.30	—	2.87	4.44	2.25	3 62
Monochloroacetic		2.87	4.98	4.78	5.63	4.00	8.81	9.04	5.77	5.34	4.48	5.32	—	—
Acetic		4.76	—	—	—	—	—	10.84	—	—	6.07	—	—	—
Formic		3.75	—	5.91	6.29	—	—	9.66	6.23	6.06	5.06	4.09	—	—
Salicylic		2.97	5.04	4.42	5.38	—	8.73	8.24	3,22	5.35	4.11	5.07	—	—
Benzoic		4.20	—	—	—	—	—	10.62	—	—	5.66	—	—	—
m-Nitrobenzoic		3.49	—	4.95	6.18	—	—	9.40	—	5.81	4.82	3.85	—	—
p-Nitrobenzoic		3.40	—	—	6.03	—	—	9.37	—	—	4.85	3.88	—	—
o-Nitrobenzoic		2.20	—	—	—	—	8.87	9.36	5.10	—	4.26	—	—	—
Picric		0.80	0.69	1.12	1.82	1.33	—	4.64	1.77	1.60	1.39	0.43	1.31	1.11
α-Nitrophenol		4.02	4.64	4.18	5.54	—	8.84	8.25	5.92	5.51	4.26	4.01	—	—
β-Nitrophenol		3.80	4.66	3.97	5.21	—	8.84	8.68	5.15	5.01	3.64	4.04	—	—
Hydrochloric		0.8		—	—	—	—	—	—	—	—	1.21	—	—
Sulphuric		—3.0	—	—	—	—	—	—	—	—	—	1.46	—	—

3. Esters

Esters are solvents which contain a carbonyl group, like ketones, but they also contain alkoxy-oxygen, that is, they have a compound functional group.

Most workers[113-117] consider that esters react with acids chiefly through the carbonyl oxygen, but some authors[114-116] conclude that reaction between the acids and the alkoxy-oxygen of the ester is also possible.

Esters form reaction products with the 1:1 composition both with acids and with nitrophenols[113]. According to Izmailov's theory, esters should be differentiating solvents. The oxygen atoms in the ester molecule, however, may be screened to some extent by the radicals, so that steric effects may be observed in the reaction with carboxylic acid dimers. It is therefore to be expected that esters with different radicals and different structures may show varying differentiating properties.

We studied the strength of acids (chiefly carboxylic acids and nitrophenols)[118-121] in eleven esters and an acetone–benzene mixture with an acetone mole fraction of 0.305 (DC = 6)[122]. The strengths of the acids were determined by the buffer-free indicator methods described above. In most of the esters with low DC which we studied, we determined the transformation constants of the acids and the indicators; in two esters with larger DC values (ethyl monochloroacetate and acetoacetic ester) we determined the dissociation constants of the acids. The results are given in Table 16.

The strengths of the acids depend on the basic strength of the solvent. The basic nature of the esters was studied by various methods: from the ionisation potentials[123-128], the solubility of HCl[59,60], the shifts in the infrared spectra on reaction with the OD group of methanol[90,92,129-132], and the Taft constants[133].

On the basis of published data, the esters which we studied can be arranged in order of decreasing basic strength. This order is given in Table 17, which also gives the values of pK for the transformation of picric and trichloroacetic acids.

Table 17.

	Esters	pK_{tr} for picric acid	pK_{tr} for trichloroacetic acid
decreasing basic nature ↓	Tributyl phosphate	0.44	3.32
	Butyl acetate	0.70	1.14
	Tricresyl phosphate	1.11	—
	Ethyl acetate	1.12	1.60
	Triphenyl phosphate	1.31	2.69
	Phenyl acetate	1.33	1.51
	Ethyl benzoate	1.60	1.92
	Diethyl carbonate	1.77	2.54
	Benzyl acetate	1.82	2.57
	Acetoacetic ester	4.65	6.28

With decrease in the basic strength of the esters there is an increase in the value of pK for picric acid, that is, a decrease in its strength (Table 17). This relationship is not observed for trichloroacetic acid. For example, in the most basic ester—tributyl phosphate—pK_{tr} for trichloroacetic acid is greater than the values in other esters which are less basic. Thus the change in the strength of nitrophenols in esters is related chiefly to the basic nature of these solvents, whereas the strengths of carboxylic acids are determined not only by the basic nature of the ester, but also by other factors.

In all esters, the decrease in the strengths of carboxylic acids on going from water to the ester is greater than the decrease in the strengths of the nitrophenols. This characterises the esters as differentiating solvents. The differentiating action of esters is illustrated by Table 18, which gives the $\Delta' pK$ values determined graphically from the data in Table 16. The results show that the differentiating action of the esters which we studied on the strength of acids varies between different esters (Table 18). The differentiating action of esters does not depend on their dielectric constant.

Although the esters of acetic acid have similar dielectric constants, their differentiating properties differ considerably. The differentiating action of diethyl carbonate—an

ester with low dielectric constant—on the strength of acids is similar to that of ethyl acetate—a solvent with high dielectric constant. Acetoacetic ester, with high DC, is a strongly differentiating solvent.

Examination of Table 18 shows that the differentiating properties of esters depend on the nature and spatial complexity of the radical of the alcohol group.

Table 18. Differentiating action of esters.

Solvents	DC	$\Delta' pK_{tr}$	Solvents	DC	$\Delta' pK_{tr}$
Butyl acetate	5.01	2.0	Benzene + acetone	6.02	1.2
Benzyl acetate	5.10	1.4	Tributyl phosphate	7.97	3.2
Ethyl acetate	6.02	1.6	Triphenyl phosphate	—	1,4*
Phenyl acetate	5.35	0.6			$\Delta' pK$
Diethyl carbonate	2.82	1.6	Acetoacetic ester	15.70	2.0
Ethyl benzoate	6.02	1.2	Ethyl monochloroacetate	20.00	0.8

* Estimated from data in Table 17.

The data in Table 16 show that the strengths of carboxylic acids in esters of acetic acid decrease with increase in the spatial complexity of the alkoxy-radical. In accordance with this, the differentiating properties of these solvents decrease in the order: butyl acetate > ethyl acetate > benzyl acetate > phenyl acetate. Thus the reaction of carboxylic acids with esters is influenced by steric effects depending on the size and complexity of the alkyl radical.

Ethyl acetate and diethyl carbonate exhibit the same differentiating action on the strengths of carboxylic acids and nitrophenols. It may be assumed that the identical differentiating action is determined by the identical degree of screening of the functional groups of the ester in these compounds.

Ethyl benzoate is a slightly weaker differentiating solvent than diethyl carbonate and ethyl acetate, since its acidic group contains the planar phenyl radical. Ethyl monochloroacetate is a weak differentiating solvent. This can apparently be attributed to the reduced electron-donating power of its functional group associated with the presence of the chlorine atom in its molecule[134,135].

The data in Table 16 show that the strengths of not only carboxylic acids, but also nitrophenols, are low in ethyl monochloroacetate, compared with ethyl acetate and other esters of carboxylic acids. We also studied the differentiating properties of acetoacetic ester (Table 16), which under ordinary conditions contains keto- and enol-forms. In pure acetoacetic ester under normal conditions, the keto form predominates (93%). This ester is a strongly differentiating solvent (Table 18). We purified acetoacetic ester in an all-glass distillation apparatus. These distillation conditions, and also the addition of acids, displace the equilibrium towards the formation of the enol form. In the liquid state, as a result of intramolecular hydrogen bonding, the enol form is present as a chelate compound[136] in which there is particularly strong steric hindrance to the reaction with carboxylic acid dimers. This is apparently also responsible for the differentiating properties of acetoacetic ester.

Esters of phosphoric acid can be arranged in the following order of decreasing differentiating properties: tributyl phosphate > tricresyl phosphate > triphenyl phosphate. The fact that tributyl phosphate has the strongest differentiating action can be attributed to the spatial complexity of its molecule, resulting from the large butyl radicals arranged at the apices of a tetrahedron[137,138]. In triphenyl phosphate the planar phenyl radicals also lie at the apices of a tetrahedron, but in contrast to the situation in tributyl phosphate, the axes of the phenyl radicals are parallel to one another[139]. This is apparently responsible for the fact that the steric hindrance to the reaction with carboxylic acid dimers is less for triphenyl phosphate than for tributyl phosphate.

Tributyl phosphate exhibits specific differentiating properties. Differentiation within the class of carboxylic acids is observed in this solvent: the chloroacetic acids are weaker than the nitrobenzoic acids. The behaviour of mineral acids in tributyl phosphate is also unusual: in this solvent, hydrochloric and sulphuric acids are weaker than picric acid[120]. In accordance with published data[140,141], we regarded sulphuric acid in tributyl phosphate as a monobasic acid. The transformation constants which we obtained[120] by the indicator method for hydrochloric and sulphuric acids in tributyl phosphate are close to one another. Hesford and McKay[142] determined the dissociation constants of these acids in tributyl phosphate from their electrical conductivities. The values which they obtained are also close to one another. The first dissociation constant of sulphuric acid was calculated.

The replacement of the butyl radicals by cresyl or phenyl radicals in the phosphoric acid ester leads to a decrease in the differentiating power of the solvent.

The stronger differentiating action of the esters of phosphoric acid compared with the esters of acetic acid can be attributed both to the structure of the molecules of the phosphoric acid esters and to the nature of phosphoric acid. The molecules of the esters of phosphoric acid have a tetrahedral shape, in which one of the apices is occupied by the phosphoryl oxygen, whereas the molecules of the esters of acetic acid have a planar structure, with *cis*-arrangement of the radicals[143].

Table 19. Integral heats of dissolution of salts[120,121] at a dilution of 1:400 (27°C).

Diethylammonium salts	ΔH, kcal mole^{-1}		
	water	benzyl acetate	tributyl phosphate
Picrate	4.8	5.0	3.1
β-Dinitrophenolate	4.7	6.9	2.5
Benzoate	insol.	2.5	10.9
Salicylate	2.8	4.0	3,8
Trichloroacetate	1.8	6.6	6.8
Acetate	—0.8	3.9	9.1

To estimate the influence of the solvation of the anions of the acids by different esters on the differentiating properties of the latter, we determined the integral heats of dissolution of the diethylammonium salts of various carboxylic acids and nitrophenols in benzyl acetate (a weakly differentiating solvent) and tributyl phosphate (the strongest differentiating solvent)[120,121]. The results (Table 19) show that the solvation of the anions of carboxylic acids in esters is much more endothermic than that in water. The solvation of the anions of nitrophenols in benzyl acetate is

slightly less exothermic than that in water, whereas in tributyl phosphate the opposite relationship is observed.

Comparison of the heats of solvation of the anions of the acids in the two esters (Table 19) indicates that the difference in the differentiating action on the strength of acids shown by tributyl phosphate and benzyl acetate is related not only to the factors examined above but also to a difference in the solvation of the anions of the carboxylic acids. The decrease in the solvation of the anions of the carboxylic acids in tributyl phosphate can be attributed to steric effects in the reaction of these anions with the ester.

Thus the differentiating action of esters depends on steric effects produced in the reaction of their molecules with both the molecules and the anions of carboxylic acids.

On the basis of our studies, esters can be recommended as differentiating solvents for the titration of acids.

Tributyl phosphate is a specific differentiating solvent. Picric acid and trichloroacetic acid can be determined separately in the presence of one another in this solvent. In this solvent it is also possible to determine separately chloroacetic and nitrobenzoic acids, which have similar strengths in water. This has been confirmed by our experiments [121] on colorimetric and high-frequency titration.

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The change in the strength of acids of different character on going from water to oxygen-containing solvents (alcohols, ketones, ethers, and esters) depends on steric effects in the reaction of the molecules and anions of the acids with the solvent molecules. Increase in the spatial complexity of the solvent molecules and increase in the screening of the oxygen of the functional group lead to a relative decrease in the strengths of carboxylic acids; this is responsible for the differentiating action on the strength of acids in a given solvent.

Steric factors are particularly important in the reaction of carboxylic acid dimers with the alkoxy-oxygen of the solvents (alcohols and ethers).

The differentiating action of primary alcohols depends little on the size and degree of branching of their radical. Secondary and tertiary alcohols have a stronger differentiating action on the strength of acids than primary alcohols.

Ethers with sterically simple radicals (diphenyl oxide and anisole) are almost levelling solvents. The differentiating action of ethers with saturated radicals on the strength of acids increases considerably with increase in the size and complexity of their radicals.

The difference in the strengths of carboxylic acids in solvents containing alkoxy-oxygen is determined not so much by the basic nature of the solvent and hence the strength of the hydrogen bond formed as a result of the reaction of the carboxylic acid dimers with the molecules (in the case of alcohols, with the molecular associates) of the solvent as by the probability of formation of this bond, which depends on steric factors.

Ketones and esters are differentiating solvents, but the differentiating properties of these compounds also depend on the spatial complexity of their molecules and are determined by the relative decrease in the strength of carboxylic acids in these solvents.

Examination of the behaviour of the acids which we have studied in oxygen-containing solvents leads to the general conclusion that the strengths of acids in solvents depend on the spatial complexity of both the molecules and the ions of the acid and the molecules of the solvent. The differentiating properties of a solvent are determined to a considerable extent by steric effects in the reaction of the electrolyte with the solvent.

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Active Centres in the Polymerisation of Hydrocarbon Monomers by Anionic Coordination

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Several aspects are discussed of the nature and character of the active centres in the polymerisation of diene hydrocarbons (mainly butadiene) initiated by organic compounds of alkali metals or by cobalt and nickel complexes. Such polymerisations occur by a complicated mechanism of anionic coordination, characterised by the presence of active centres in the form of polarised bonds between carbon and metal atoms (the alkali metals and the transition metals in the complexes). The coordinating and anionic functions of the active centres, their combination, and mutual transitions are discussed for the polymerisation of butadiene and other hydrocarbon monomers in the presence of organic compounds of alkali metals.
The Section on polymerisation initiated by complex cobalt catalysts reports research on the role of small amounts of water in the formation and breakdown of the initial active centres. The last Section examines the formation of active centres from complexes of the π-allylnickel halide type and the mechanism of their participation in the polymerisation of butadiene

CONTENTS

I. Introduction 834
II. Nature of active centres in polymerisation in the presence of organic compounds of alkali metals 834
III. Active centres in the polymerisation of butadiene in the presence of complex catalysts based on cobalt and nickel 838

I. INTRODUCTION

Great attention has recently been paid to problems of polymerisation by ionic coordination, because of the wide possibilities it offers for the directed control of the composition and the structure of the polymer chains. However, the study of these processes—especially those which occur in the presence of complex catalysts containing transition metals in various states and combinations—encounters considerable theoretical and experimental difficulties.

An approach which will bring us closer to an understanding of several fundamental aspects of these systems, in particular problems associated with the nature of the active centres of chain propagation, may be to investigate polymerisation in the presence of alkali metals and their organic compounds. These processes represent simpler systems, but cover a wide range of phenomena, while allowing the structure of the active centres to be varied in a known manner, and thereby enabling various types of configuration and relative arrangement of the monomeric units to be realised in the growing polymer chains. In this sense they can serve as simplified models for the discussion of more complicated catalytic polymerisation systems.

Polymerisation in the presence of an alkali metal (sodium) was first used in 1932 in the Soviet Union to obtain synthetic butadiene rubber on the industrial scale by S. V. Lebedev's method.

In 1936 the first kinetic investigation, which used a vacuum technique, was published[1] on the vapour-phase polymerisation of butadiene on thin films of metallic sodium deposited on the walls of the reaction vessel. This work established that polymerisation takes place in a layer of butadiene which deposits on the walls of the vessel (Fig. 1).

The induction period is due to the presence of unchanged metallic sodium (initiation reaction). After the metallic mirror has disappeared, the process occurs at a constant rate. Prolonged interruption of the process (by pumping off the butadiene) with subsequent introduction of butadiene to the appropriate pressure did not affect the rate of polymerisation.

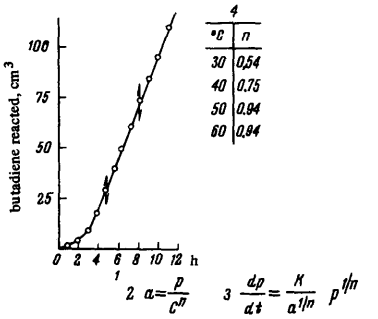


Figure 1. Gas-phase polymerisation of butadiene on metallic sodium mirrors:
1) dependence of conversion of butadiene on time at constant pressure p (the arrows denote interruptions); *2*) a = partition coefficient of butadiene between gas and polymer phases; *3*) rate of polymerisation at constant volume; *4*) dependence of coefficient n on temperature*.

* Curves *2* and *3* have apparently been overlooked (Ed. of Translation).

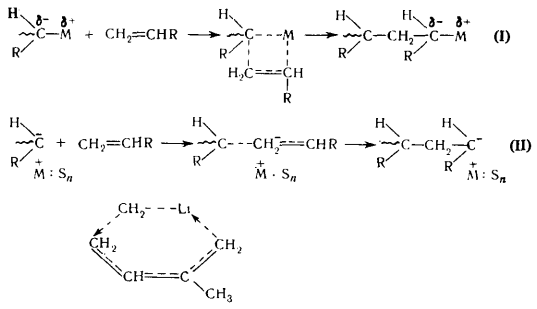
These experiments revealed a novel type of active centre for the growth of polymerisation chains, distinguished by the absence of chain termination and by thermodynamic stability. It was assumed that chain growth took place by incorporation of the monomer in the carbon–sodium bond. These phenomena were subsequently interpreted in terms of "chain catalysis" [2]. In present-day terminology—which is admittedly not perfect—these centres, the first to be discovered, can be termed "live" active centres.

II. NATURE OF ACTIVE CENTRES IN POLYMERISATION IN THE PRESENCE OF ORGANIC COMPOUNDS OF ALKALI METALS

As was mentioned above, the scientific interest and practical value of these processes are due to the presence of a definite relation between the nature of the initiator

(catalyst) and the structure of the active centres for chain growth, which in turn determine the composition, structure, and dimensions of the polymer chains, and to considerable extent the properties of the resulting polymers.

Many research papers have appeared[1-40] on these processes, and the results together with other published data enable the characteristics of the reactions of chain growth to be established. These characteristics can be represented by the scheme



where M is an alkali metal. Two types of active centres for chain growth are shown, differing in the nature of the C–M bond, which determines the rate of the elementary acts of growth and coordination of monomer units in the growing chains.

In the first type the active centres consist of polarised C–M bonds, in which covalent (exchange) forces play an important part. The transition state in reactions of chain growth may be supposed in this case to be a four- or six-membered ring (for vinyl or diene monomers respectively). The metal atom is directly involved in the growth reactions. The two-centre character of the active group determines the system of coordination of a monomer unit in the growing chain. For this reason we shall term this type of process the *coordination mechanism* of the growth of polymer chains.

The second type of active centre is characteristic of chain-growth reactions occurring by an *anionic mechanism*. Increasing polarisation of the C–M bond results in charge separation, depending on the nature of the alkali metal and the properties of the medium: only a certain Coulombic interaction is preserved between the carbanion and the counter ion, an *ion-pair* being formed. In this case the transition state of the growth reactions has a linear structure (one-centre type of active group), and the coordinating effect of the counter ion is small. With further weakening of electrostatic interaction between the ion and the counter ion under the influence of solvation of the latter by strong electron-donor solvents, *free carbanions* are produced. Processes occurring on ion-pairs with complete separation of charges and on free ions may be supposed to involve transition states of analogous structure. The difference is probably that with ion-pairs the growth reactions had to be inhibited by the fact that the solvated counter ion must move along the growing chain.

Actual polymerisation processes initiated by alkali metals and their organic compounds combine in most cases features of both mechanisms, and are processes of *anionic–coordination polymerisation*.

The term "mechanism" may lead to a wrong idea of the essential nature of these processes. It must not be thought that two different types of centres are involved, one of which is responsible for the occurrence of the process by an anionic mechanism, while the other causes polymerisation by a coordination mechanism. The essential point is that the same active centre possesses both anionic and coordinating functions at the same time, but they are combined to different extents depending on the nature of the metal, the properties of the medium, and the temperature. In the limit the predominance of one function or the other may result in either an anionic or a coordination mechanism.

A characteristic feature of processes of anionic–coordination polymerisation is the presence of a reactive C–M bond in the growing chains, the state of this bond—primarily its degree of polarisation—determining the possible relative importance of anionic and coordination mechanisms, the overall rate of the process, and the composition and structure of the polymer chains. Decrease in the degree of polarisation of the C–M bond is accompanied by an increase in the coordinating power of the alkali metals in the active centres. With a given monomer in the absence of electron-donor compounds, this increase in the coordinating factor varies in parallel with the ionisation potentials of the alkali metals:

$$\begin{array}{ccccc} K & < Na & < Li \\ 4.32 & 5.09 & 5.37 \end{array}.$$

Another important characteristic of metals in active centres, affecting the degree of polarisation of the C–M bond, is the presence of vacant orbitals in the metal atoms, as also the ionic radii determining their electron-acceptor properties. The lower the vacant orbitals and the smaller the ionic radii, the stronger is the solvation (or complex formation) of the metal atoms by electron-donor solvents

$$\sim CH_2\overset{\delta-}{C}H-\overset{\delta+}{M} + nS \rightarrow \sim CH_2\overset{\delta_1-}{C}H-\overset{\delta_1+}{M}:S_n$$
$$\qquad\qquad R \qquad\qquad\qquad\qquad R$$

where $\delta_1 > \delta$ and S is an electron donor. Solvation tends to increase the polarity of the C–M bond and also the proportion of the anionic process. The coordinating power of metals in active centres falls in the same sequence as the atomic radius of the metals decreases:

$$\begin{array}{ccccc} Li & > Na & > K \\ 0.6 & 0.95 & 1.33 \end{array}.$$

The simultaneous development of anionic and coordination mechanisms can be conveniently examined with the anionic–coordination polymerisation of butadiene as example, this leading to the formation of polymer chains containing monomer units differing in structure (1,2, *cis*-1,4, and *trans*-1,4). Table 1 shows that, in hydrocarbon solvents, where solvation of the counter ion† by the monomer is negligible, the coordinating power of the counter ion is most clearly apparent in lithium active centres, the preferential formation of 1,4-polybutadiene. With sodium and potassium centres the extent of participation of the coordinating factor in chain growth diminishes in the sequence K < Na < Li, this being accompanied not only by formation of 1,2-structures but also by decrease in the relative content of *cis*-1,4-structures in the polybutadiene chains. The relative content of *trans*-1,4-structures remains almost constant.

The introduction of an electron-donor compound, which causes solvation of the counter ion, increases the importance of the anionic process (formation of 1,2-structures). These effects are especially marked in the presence of lithium centres, are weaker with sodium centres, and are weak in the presence of potassium centres, in conformity with the solvation sequence Li > Na > K, as is evident

† For simplicity we shall henceforth term C in the C–M bond the anion, and M the counter ion, independently of the mechanism of the process.

from Table 1, which gives experimental results for the addition of triethylamine (TEA, a weak electron donor) and tetrahydrofuran (THF, a strong electron donor). Lowering the temperature, by favouring solvation of the counter ion, increases the role of the anionic factor. In pure tetrahydrofuran, owing to the breakdown of covalent (exchange) interaction between the carbanion and the counter ion, chain growth takes place on *ion-pairs*. Differences associated with the nature of the alkali metals are then smoothed out, and the mechanism of the process becomes predominantly anionic (preponderant formation of 1,2-structures).

Table 1. Effect of conditions of polymerisation on structure of polybutadiene[18].

Metal in bond	Medium	Addition		Temp., °C	Structure of polybutadiene, %		
		cpd.	%		1,2	*cis*-1,4	*trans*-1,4
Li	heptane	—	—	30	6.8	42.8	50.4
Li	toluene	—	—	30	8.7	43.7	47.6
Na	benzene	—	—	25	32.3	22.6	45.0
Na	toluene	—	—	25	31.5	23.1	44.8
K	benzene	—	—	25	35	16.5	48.5
K	benzene–heptane (5:1)	—	—	0	38.1	12.8	49
Li	benzene	TEA	10	25	37.1	22.8	40
Na	benzene	TEA	10	25	43.3	17.3	39.4
K	benzene	TEA	10	25	37.4	16.6	46.0
Li	benzene	THF	1	25	73.6	13.3	13.1
Na	benzene	THF	1	25	44.3	12.8	42.8
Li	heptane	THF	6	—50	91.5	4.1	4.4
Na	cumene	THF	6	—50	88	—	12
K	heptane	THF	6	—50	61.6	5.1	33.3
K	cumene	THF	6	—50	58.8	5.8	35.4
K	cumene	THF	15.5	—50	61.7	5	33.3
Na	THF	—	—	—50	88	—	12
Na	THF	—	—	—90	92.8	—	7.2
K	THF	—	—	—50	84.7	—	15.3
Li	THF	—	—	—50	91	—	9

Similar results on the nature of the active centres and on the combination of anionic and coordination factors depending on the nature of the alkali metals and the properties of the medium have been obtained, in conformity with the ideas developed, in investigations of the composition of copolymers[14,15] and of chain-transfer reactions[14,29].

Examination of rates of growth in the anionic–coordination polymerisation of isoprene, butadiene, and styrene has established that these processes take place by a mechanism of "live" chains. Yet it was found that the rate of the process does not depend on the first power of the initiator concentration, as should have been the case with "live" chains, but is given by the equation

$$v = k_p[M][C]^{1/n} \qquad (1)$$

where [C] is the initiator concentration and $n > 1$ is a constant. The explanation given for these deviations was that in non-polar media the growing chains, with a polar group at the end, form stable association complexes, and these break down into non-associated growing chains in conformity with the equilibrium

$$(M-P)_n \rightleftarrows (M-P)_{n-1}M-P \qquad (2)$$

where P is the polymer chain.

The presence of association complexes in the reaction system has been confirmed by viscosimetric and spectrophotometric methods[25]. The complexes can be supposed to have either a layer or a coiled structure.

Only isolated, non-associated growing chains are active in acts of chain growth. The constant n in Eqn. (1) is a measure of the degree of association, and varies with the nature of the polymer, having values 2 for polystyrene, 3–4 for polyisoprene, and 5–6 for polybutadiene[17].

It was not possible to estimate the equilibrium constants (2) in the case of lithium centres. This constitutes the main obstacle to determining the individual growth rate constants in coordination polymerisations occurring in hydrocarbon media under the influence of alkali-metal compounds.

Several difficulties in determining chain-growth constants arise also from the isomerisation of active centres into centres of diminished activity, discovered spectrophotometrically[41,25]. However, these difficulties are eliminated by conducting the polymerisation at low temperatures (at or below −50°C).

On the introduction of electron-donor additives—tetrahydrofuran, triethylamine, etc.—into hydrocarbon media, the association complexes break down owing to solvation of the counter ions of growing chains in the complexes. Individual growing chains are then formed, with different degrees of solvation of the counter ions in the active centres depending on the electron-donor properties of the medium. The coordinating power of the C–M bond in chain-growth reactions depends substantially on the degree of solvation of the counter ions by the electron-donor compounds. These factors explain the lack of correlation between the rate of polymerisation on potassium active centres and the microstructure of the resulting polybutadienes[37].

Table 2. Effect of additions of tetrahydrofuran on the rate of chain growth in the polymerisation of butadiene and on the structure of the resulting polymers ($[M]_0 = 1$ M; initiator concentration. [KR] = 0.003 M; temperature −50°C).

Solvent	THF, total %	Rate of chain growth $10^3 v$, $M \cdot s^{-1}$	1,2-Structure, %
Cumene	—	0.0012	56
Cumene	2.7	0.012	56
Cumene	4.7	0.018	58
Cumene	20.0	0.21	64
Cumene	44.0	2.4	66
THF	—	15.6	85

Table 2 shows that the sharp changes in rate of polymerisation caused by the addition of an electron donor to the hydrocarbon medium are accompanied by slight changes in the microstructure of the resulting polymers. In view of the fact that potassium active centres form less stable association complexes and possess diminished electron-acceptor power (compared with lithium and sodium centres), this can be explained by the tendency of added tetrahydrofuran to favour formation from the association complexes of individual, non-associated growing chains, the number of which increases and causes an increase in the rate of polymerisation. However, the degree of solvation of the active centres, which affects their coordinating power, is small, and remains more or less constant as long as association complexes are present in the system. It is significant that, when the degree of solvation of the counter ions is small, covalent (exchange) forces are involved as well as electrostatic forces in the C–M bonds, and to some extent determine the proportion of the coordination mechanism in the chain-growth reactions. It is seen from Table 2 that, even in media containing 44% of tetrahydrofuran, ~ 34% of 1,4-structures are present in the polymer chains. In pure tetrahydrofuran, solvation of the

counter ion increases, covalent interaction in the C–M bonds contracts (screening of the counter ion by the solvate sheath), and the chain-growth reactions take place by an anionic mechanism.

1. Spectrophotometric Investigation of Active Centres for Chain Growth

The first spectrophotometric investigations of the C–M bond in lithium, sodium, and potassium active centres for polyisoprene, polybutadiene, and polystyrene showed that the position of the absorption band maximum λ_{max} is independent of the nature of the metal or the properties of the medium[42]. However, such dependence of the spectra has been detected in the corresponding triphenylmethyl, fluorenyl, indenyl, and 1,1-diphenylbutyl organometallic compounds (λ_{max} shifts to longer wavelengths with increase in polarity of the C–M bond)[25]. Detailed examination of the phenomena led to the conclusion that the spectra found for the first group of compounds ("live" chains of polyisoprene, polybutadiene, and polystyrene) relate not to individual growing chains but to their association complexes, which are characterised by great stability and are present in great quantity. The presence of bulky substituents in the second group of compounds and the consequent steric hindrance prevent the formation of stable association complexes, which readily break down even under relatively slight action by electron donors. Discrete transitions of active centres (the C–M bond) from one form to another depending on the nature of the medium are illustrated by the spectral pattern of 1,1-diphenylbutyl-lithium systems (Table 3).

Table 3. Ultraviolet spectra of 1,1-diphenylbutyl-lithium systems[25].

Solvent	λ_{max}, nm	Temp., °C
Hexane	410	25
Triethylamine	437	25
Hexane + 0.3% THF	440	25
Hexane + 0.3% THF	490	−80
THF	490	25

A sharp change in λ_{max} is observed on passing from hexane (unsolvated counter ions) to triethylamine or to a 0.3% solution of tetrahydrofuran (degree of solvation of counter ions small). A second transition, to completely solvated counter ions, occurs in solutions of pure tetrahydrofuran or when the temperature is lowered to −80°C, which favours solvation.

It has since been shown, by spectrophotometric combined with kinetic methods[30,17], that the degree of association and the stability of the association complexes of lithium active centres in hydrocarbon media depends on the carbanion component in the C–M bond, increasing in the sequence—1,1-diphenylethylene < α-methylstyrene < styrene < isoprene < butadiene.

It has also been established by conductometric methods that, in the polymerisation of α-methylstyrene in electron-donor solvents, the presence of steric hindrance in poly-α-methylstyrene, impeding the formation of association complexes in hydrocarbon media, promotes the dissociation of ion-pairs into free ions[40].

To elucidate the nature of the C–M bond in non-associated growing chains, spectrophotometric investigations have been made under conditions of the maximum concentration predominance of these forms, i.e. at concentrations below 10^{-5} M.[17,42,43]

Development of a special technique for spectrophotometric measurements at high dilutions with live lithium–polystyrene chains as example has shown that change in the concentration of lithium centres in toluene solution from 10^{-3} M to $\ll 10^{-5}$ M is accompanied by a shift in the absorption band maximum λ_{max} of 18 nm to shorter wavelengths. This band corresponds to non-associated and non-solvated active centres of growing chains[30].

The spectrophotometric research results cited support the earlier suggestion that in hydrocarbon media the C–M bond is a polarised bond, not an ion-pair.

2. Active Centres in Pure Electron-donor Media

It has been shown above that the metal atom in the active centres undergoes two types of interaction—with the end of the growing chain and with electron-donor molecules C...M...S_n—the relative strengths of anionic and coordination mechanisms of chain growth depending on the intensity and character of these interactions (exchange and electrostatic forces, solvation). It may be assumed that in pure and strong electron-donor media chain growth will take place solely by the anionic mechanism.

Table 4. Chain-growth rate constants in the anionic polymerisation of butadiene in different solvents, $M^{-1} s^{-1}$.[26]

Counter ion	Tetrahydrofuran						Dimethyl ether	
	+10°C	−30°C	−43°C	−56°C	−82°C	−96°C	−30°C	−56°C
Li	0.85	0.14	—	0.03	—	—	2.2	1.0
Na	5.4	1.8	1.05	0.60	0.40	0.29	23	8
K	70	17	—	3.1	—	0.16	—	16

This conclusion is to some extent confirmed by a detailed investigation of these processes[28], since the variation in the chain-growth rate constants found for the polymerisation of butadiene in tetrahydrofuran over the temperature range from +10° to −56°C corresponds to the sequence Li < Na < K, which is characteristic of an anionic mechanism (Table 4). However, the same investigations have shown that certain restrictions must be placed on this conclusion. It is seen from Table 5 that the microstructure of the polybutadiene formed in tetrahydrofuran medium depends on the temperature and the nature of the metal in the active centre of the growing chains.

The existence of such a relationship, which is shown especially clearly with potassium and caesium active centres and at relatively high temperatures, indicates that the counter ions are to some extent involved in chain growth. The type of dependence on the nature of the metal and the temperature also corresponds to processes of anionic coordination, not purely anionic processes.

In connection with the results obtained, the question arises of the formation of free ions and the part they play in these processes. The decisive role of free ions in the polymerisation of styrene in electron-donor media has been established by Szwarc[44] and by Schulz[45]. However,

the fact that the polymerisation of butadiene under analogous conditions follows the rules of anionic coordination throws considerable doubt on the role of free ions in this system. In fact, direct conductometric examination of these systems not only has strengthened these doubts but has led to the opposite conclusions[33].

Table 5. Microstructure of polybutadiene obtained in tetrahydrofuran[26,32].

Counter ion	Structure,%*	Temperature, °C				
		+40	+10	−30	−56	−96
Li	1	84.0	85.9		91.0	
	2	8.4	7.6	—	9.0	—
	3	7.6	7.2		0	
Na	1		79.3	82.9	88.0	92.7
	2	—	15.5	15.6	12.0	7.3
	3		5.2	1.5	0	0
K	1	56.6	63.5	76.4	83.5	88.3
	2	36.5	30.4	20.7	14.8	11.7
	3	6.7	6.1	2.9	1.7	0
Cs	1		60.6	72.7	82.9	89.0
	2	—	31.4	27.3	17.1	10.9
	3		8.0	0	0	0

* 1 = 1,2-structure; 2 = *trans*-1,4; 3 = *cis*-1,4.

One piece of evidence for the decisive role of free ions in the polymerisation of styrene has been the correspondence between kinetic and conductometric results[44]. However, such correlation has been found to be completely absent in the polymerisation of butadienes[33]: the reactivity of the active centres increases according to the nature of the counter ion in the sequence Li < Na < K (see Table 4), whereas the ability of the centres to dissociate into free ions increases in the opposite sequence K < Na < Li (Table 6).

Table 6. Dissociation constants of live polymers at 25°C ($10^7 K_{diss}$, M).[33]

Counter ion	Carbanion				
	butadiene	styrene	anthracene	butadiene	styrene
	Tetrahydrofuran			Dimethyl ether	
Li	0.85	1.7	—	31	43
Na	0.82	1.0	9.0	5.5	22
K	0.55	0.58	—	2.2	3.2

Thus in electron-donor media the behaviour of active centres in the polymerisation of butadiene is determined not by free ions, although their concentration in these systems is comparable with the concentrations in the case of styrene, but by ion-pairs. This conclusion is further supported by the fact that addition of potassium tetraphenylborate, which lowers the concentration of free carbanions, does not affect the rate of polymerisation of butadiene or the microstructure of the polybutadiene.

Hence it follows that results obtained with one monomer cannot be extended to other monomers without first carefully studying their behaviour, for, as has been shown with butadiene and styrene, different results are obtained depending on the nature of the monomer.

III. ACTIVE CENTRES IN THE POLYMERISATION OF BUTADIENE IN THE PRESENCE OF COMPLEX CATALYSTS BASED ON COBALT AND NICKEL

It has been established above that, in the polymerisation of hydrocarbon monomers, the active centres for growth of polymer chains can be of different types—covalent bonds of various degrees of polarisation, ion-pairs, and free ions—depending on the nature of the alkali metals, the proporties of the medium, and the temperature. The structure of complex catalytic systems containing transition metals is, of course, considerably more complicated, and development of their properties is more diverse than with the alkali metals. The ability of transition metals to exist in different states of oxidation, their tendency to various types of complex formation (σ-, π-, and n-complexes), donor–acceptor interaction, and the varied configuration of the complex systems create a certain boundary between the behaviour of the alkali metals and that of the transition metals in processes of ionic–coordination polymerisation.

Nevertheless, these two types of processes exhibit several common features, and therefore the generalisations applicable to ionic–coordination polymerisation occurring in the presence of alkali metals and their organic compounds may serve as an approach to the consideration of the more complicated type of processes, as remarked at the beginning of the paper.

Many published studies of the polymerisation of hydrocarbon monomers (in particular of butadiene) in the presence of complex cobalt and nickel catalysts indicate that the active centres for growth of the polymer chains are $C^{\delta-}-M^{\delta+}$ bonds (where M represents the transition metal) polarised in the direction characteristic of anionic–coordination processes. The degree of polarisation of this bond depends on the structure of the bimetallic complex, the nature of the ligand, the transition metal, and the properties of the medium. The formation of ion-pairs and especially of free ions in these processes, occurring in non-polar hydrocarbon media, is improbable. Certain kinetic features of these systems will be further considered from this point of view.

In many investigations on processes of this type no clear distinction is made between homogeneous and heterogeneous processes, despite the fact that the structure of the active centres and their development in acts of chain growth depend fundamentally on the properties of the reaction media.

The present paper discusses only processes taking place in homogeneous—mainly hydrocarbon—media. Since these processes are extremely sensitive to various impurities, which when present in minute quantities affect polymerisation, and are sometimes difficult to determine by the usual analytical methods, procedures have been developed for purifying the starting materials and also a vacuum dilatometric method, which practically eliminate their presence in the reaction medium and their influence on the processes under investigation.

1. Polymerisation of Buta-1,3-diene in Benzene Solutions in the Presence of the Complex System $CoPy_2Cl_2 + R_2AlCl$

A considerable amount of work has been done[46–51] on the polymerisation of buta-1,3-diene in the presence of complex "cobalt" catalysts, with many interesting observations and several hypotheses on their mechanism. In particular, it has been shown that these processes involve the

formation of polybutadiene chains in which *cis*-1,4-units greatly preponderate (95–98%), this being characteristic of a coordination mechanism.

Nevertheless, many fundamental questions associated with the behaviour of active centres in the systems still remain unanswered, and attempts to settle them have led to contradictory results. Researches with the aim of helping to fill this gap have been conducted in the Lomonosov Moscow Institute of Fine Chemical Technology[34,52-54]. These investigations of the polymerisation of butadiene in the presence of a catalytic system comprising $CoPy_2Cl_2$ and R_2AlCl (where Py represents pyridine, and R isobutyl or ethyl) have established an extremal dependence of the initial rate of polymerisation and increase in molecular weight of the polymers on the concentration of water added in small amounts to the initial reaction mixture. However, the small number of experiments and the order in which water was added in these investigations did not permit accurate determination of the actual concentrations of added water or the corresponding positions of the maxima on the plot of initial rate of polymerisation against initial concentration of water.

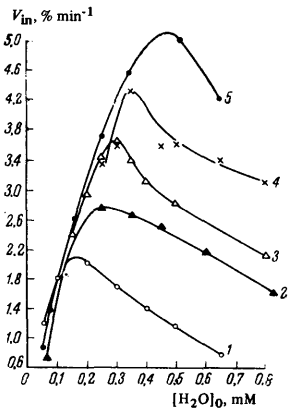


Figure 2. Dependence of initial rate of polymerisation of 1.56 M butadiene on initial concentration of water at 21°C with $[Al]_0/[Co]_0 = 400$ and cobalt concentrations ($[Co]_0$, mM) of:
1) 0.010; *2*) 0.012; *3*) 0.014; *4*) 0.017; *5*) 0.020.

Further examination of these systems by Volkov[55] using an improved dilatometric method has led not only to a more exact determination of the initial concentration of water and the corresponding position of the maxima but also to the possibility of assessing the main features of these processes associated with the properties of the active centres under various conditions. However, the main problem of the structure of the initial complex and its active forms could not be solved unambiguously even in these investigations, owing to the need to conduct the processes at extremely low concentrations and to the instability of the complex system during polymerisation.

In particular, the instability of the initial pure catalytic system is shown by the fact that the polymerisation of butadiene proceeds at a negligible rate, forming a polymer of low molecular weight, and after 2–3% conversion it stops completely. Separate experiments have established that irreversible breakdown of the whole catalytic system has occurred.

On the addition of water the rate increases sharply over the concentration range 0.05–0.8 mM, passes through a maximum, and then falls slowly. The molecular weight of the resulting polymer increases with increase in the initial concentration of water.

These phenomena are illustrated in Fig. 2, which shows the dependence of the initial rate of polymerisation V_0 on the initial concentration of water $[H_2O]_0$ for various initial concentrations of the complex cobalt catalyst $[Co]_0$ at a constant butadiene concentration of 1.56 M and a temperature of 21°C. The ratio between the aluminium and the cobalt components of the combined catalyst was also maintained constant at $[Al]_0/[Co]_0 = 400$. It was shown that, provided that this ratio exceeds 200, further increase in $[Al]_0$ has no effect on the rate of polymerisation[56]. The phenomena illustrated in Fig. 2 therefore depend solely on the initial concentrations of the cobalt component of the catalyst $[Co]_0$ and of the added water $[H_2O]_0$.

It must be remarked that Fig. 2 represents only those reactions which start and are complete in the initial stage of the process and which are very rapid. Among them are formation of the catalytic complex from the initial components, interaction of cobalt complex with water, initiation of the monomer, and reactions leading to a fall in rate after the system has reached the maximum rate of polymerisation V_{max}.

It is evident from Fig. 2 that water tends to favour both formation of an active catalytic system and increase in its activity by increasing the concentration of active centres produced from the initial catalyst as the concentration of added water increases. When the maximum rate of polymerisation is reached, the active centres acquire their greatest stability. Further increase in $[H_2O]_0$ leads to irreversible breakdown of the active centres, which may be supposed to involve their hydrolysis. The conditions under which the maximum rate of polymerisation is reached are listed in Table 7.

Table 7. Conditions for maximum rates of polymerisation.

$[Co]_0$, mM	$V_{0,max}$, % min^{-1}	10^3k, M^{-1} min^{-1}	$[H_2O]_{0,max}$, mM	$\alpha = \frac{[H_2O]_{0,max}}{[Co]_0}$
0.010	2.20	0.55	0.16	16.0
0.012	2.80	0.51	0.25	20.8
0.014	3.65	0.56	0.30	21.4
0.017	4.30	0.56	0.35	20.6
0.020	5.05	0.53	0.45	22.50
				Mean = 21.4

The highest rates of polymerisation and the greatest stability of the active centres are governed by a constant ratio of the initial concentrations of water and the cobalt complex of

$$[H_2O]_0/[Co]_0 = \alpha = 21.4.$$

It follows from Table 7 that the rate of polymerisation in the neighbourhood of the maximum is

$$V_{max} = K_{gr} \cdot K' ([Co]_0 [H_2O]_0)^{1/2} [M]_0,$$

while the concentration of active centres is

$$[\overset{*}{Co}]_{max} = K' ([Co]_0 [H_2O]_0)^{1/2}.$$

Table 7 includes values of the rate constant, which is given by the product $K = K_{gr}K'$.

Polymerisation involving fractional powers of the initiator concentration is not altogether usual with processes in which complex catalysts take part. It is true that a similar relationship is observed when organic compounds of the alkali metals are used as catalysts, and has recently been found (see next subsection) in the polymerisation of butadiene under the influence of π-allyl complexes of nickel. In all these cases the catalyst is associated, being present in particular as dimers, and only their dissociation products possess active properties. It is possible that analogous phenomena take place in the present case.

Thus the highest concentration of initial active centres occurs in the region of the maximum (Fig. 2). The fact that fall in the initial rate of polymerisation following the maximum is due to decrease in the number of initial catalytic centres—not to termination of the growing chains—follows from the linear increase in the molecular weight of the polymers in this region (see below).

It may be supposed that the irreversible breakdown of the initial active centres is due to hydrolytic reactions, when water is present in the system in concentrations exceeding the possible increase in the number of active centres. Hence it follows that decomposition is caused by the excess of water $[H_2O]_0 > [H_2O]_{max}$.

Water has been regarded above as taking part directly in all interactions with the cobalt centre of the catalytic complex. However, the presence of R_2AlCl in large excess can hardly be of no consequence with respect to water. On the other hand, keeping a solution of R_2AlCl, water, and butadiene in benzene under the conditions of the maximum following addition of $CoPy_2Cl_2$ produced no change in the process of polymerisation. This indicates that no bonding of water into any stable compounds occurs as a result of interaction of water with R_2AlCl, but a few unstable active compounds, of enhanced electron-acceptor ability, may be formed, e.g.

$$R_2Al\overset{\delta-}{\underset{OH}{\overset{Cl}{<}}}\cdots\overset{\delta+}{H}.$$

As noted earlier, hydrolytic reactions occur at concentrations of water exceeding $[H_2O]_{max}$, and these affect also the R_2AlCl. However, the stable products are inactive towards polymerisation. Several investigators regard aluminium oxide as having an activating function[57]. However, replacement of water by an equivalent amount of aluminium oxide diminished the activity of the catalytic system, and the process ceased at 8–10% conversion.

It follows from the above facts that rapid formation of active centres takes place at the very start of the process, on mixing the initial components, their concentration being determined, it may be supposed, by the further development of polymerisation with time.

This hypothesis is supported by kinetic data obtained under conditions of the maximum $[H_2O]_0 = \alpha[Co]_0$ and with excess of water $[H_2O]_0 > \alpha[Co]_0$. It is seen from Fig. 3 that the rate of polymerisation is actually almost constant up to 30% conversion (curves *3–5*), whereas curves *1* and *2*, obtained in experiments with $[H_2O]_0 < \alpha[Co]_0$, show a fall in rate with time, which indicates that processes leading to breakdown of the active centres occur in these systems.

These phenomena, occurring with small additions of water, can be explained by the decrease with time in the number of initially formed active centres—equivalent in number to $K'([Co]_0[H_2O]_0)^{\frac{1}{2}}$—owing to distribution of the water among the many cobalt centres free from water, which causes instability of the catalytic system as a whole. The development of instability of the system in the range up to the maximum, accompanied by decomposition of the catalyst, can be illustrated by the results plotted in Fig. 4. Curve *1* shows the dependence of the percentage conversion on the time. The spontaneous breakdown of active centres in the catalyst, which is responsible for the decrease in the rate of polymerisation with time, is described by a unimolecular law.

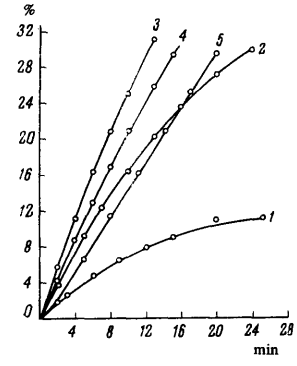


Figure 3. Dependence of percentage conversion of 1.56 M butadiene on time at 21°C with $[Co]_0 = 0.012$ mM, $[Al]_0/[Co]_0 = 400$, and concentrations $[H_2O]_0$ (mM):
1) 0.06; *2*) 0.12; *3*) 0.25; *4*) 0.60; *5*) 0.80.

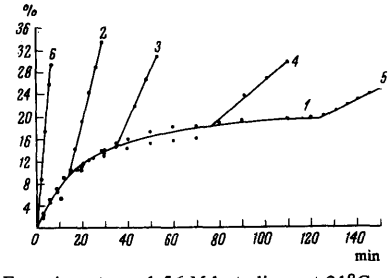


Figure 4. Experiments on 1.56 M butadiene at 21°C with $[Co]_0 = 0.017$ mM, $[H_2O]_0 = 0.05$ mM, and 0.30 mM H_2O added during polymerisation, after (min):
1) no water added; *2*) 15; *3*) 35; *4*) 75; *5*) 125; *6*) 0 (i.e. $[H_2O]_0 = 0.35$ mM, corresponding to $[H_2O]_{max}$).

The straight lines *2–5* in Fig. 4 represent the kinetic effects due to the addition of water in amounts such that its total concentration would equal that corresponding to the conditions of the maximum and described by the straight line *6*. These results show that (1) the rate of processes occurring on the introduction of water at various stages in polymerisation is lower than the maximum rate, although the total added water corresponds to that for the maximum; (2) the rate of these processes falls with increase in the time of introduction of the additional amounts of water; and (3) the rate of freshly occurring processes is constant with time, as is that of the processes occurring in the presence of excess of water, which indicates transition of the initial system from the condition $[H_2O]_0 < \alpha[Co]_0$ to the condition $[H_2O]_0 > \alpha[Co]_0$.

The above generalisations apply to the polymerisation of butadiene, the rate of which is determined by the concentration of the initial active centres, not by chain growth or chain termination. In the region of the maximum, where the system acquires its greatest stability, the rate of polymerisation during the process depends solely on the first power of the varying concentration of the monomer.

The mean molecular weight of the polymers $\overline{M}_\eta$ increases with increase in the concentration of initial water $[H_2O]_0$ and is independent of the extent of polymerisation. Fig. 5 shows that $\overline{M}_\eta$ is a linear function of the initial concentration of water, the major part of the graph relating to the region following the maximum, i.e. to the region in which the rate of polymerisation falls. These results, together with those cited earlier, show that chain termination does not occur in the course of polymerisation, but chain-transfer reactions are clearly evident, and determine the molecular weight of the polymers formed.

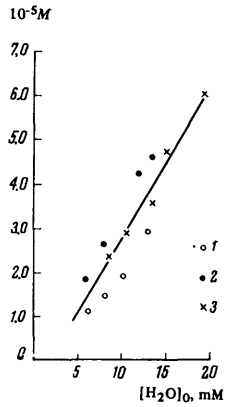


Figure 5. Dependence of molecular weight of polymers on initial concentration of water at 21°C with initially 1.56 M butadiene, $[Al]_0/[Co]_0 = 400$, and concentrations ($[Co]_0$, mM): *1*) 0.010; *2*) 0.012; *3*) 0.017.

Timofeeva [56] has studied the nature of the carrier for the growing chains.

These investigations have established that, with constant initial concentrations $[H_2O]_0$ and $[Co]_0$, the dependence of the reciprocal of the molecular weight on the initial concentration $[R_2AlCl] = [Al]_0$ is described, over a wide range of concentrations, by the relation

$$\frac{1}{\overline{M}_\eta} = a[Al]_0 + C$$

where a and C are constants. These results are consistent with Fig. 5, which shows that the increase in $\overline{M}_\eta$ with increase in $[H_2O]_0$ is smaller the greater the initial concentration $[Al]_0$.

Thus the mean molecular weight of the polymers depend on two factors—(1) interaction with R_2AlCl, which favours chain transfer, and (2) the effect of $[H_2O]_0$, which promotes chain propagation—the ratio $[Al]_0/[H_2O]_0$ reflecting the effect of the two factors, acting in opposite directions, on the molecular weight of the resulting polymers. The reciprocal of the mean degree of polymerisation $\overline{P}_\eta$ can be written

$$\frac{1}{\overline{P}_\eta} = \frac{K_{tr}[Al]_0}{K_{gr}[H_2O]_0}[M]_0$$

where K_{tr} and K_{gr} are constants representing chain transfer and chain propagation respectively. Fig. 6 shows that the direction in which $\overline{M}_\eta$ varies with the initial ratio $[Al]_0/[H_2O]_0$ corresponds to the above equation.

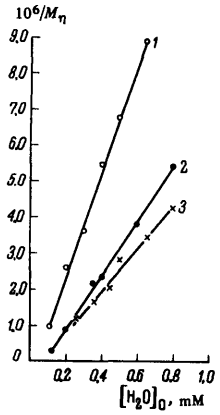
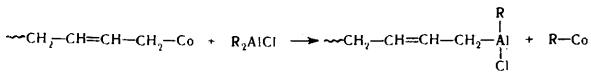


Figure 6. Dependence of $1/M_\eta$ on the ratio $[Al]_0/[H_2O]_0$ under the same conditions as for Fig.5.

The activity parameters of the bond $C^{\delta-}-M^{\delta+}$, on which the microstructure of the polymer chains depends, exhibit considerable stability: under all the conditions employed, polymers containing an overwhelming preponderance (~ 98%) of *cis*-1,4-units are formed, with the exception of polymers of low molecular weight, produced when this catalytic system is used in the absence of water. In the latter case the molecular chains comprise 74.2% of *cis*-1,4-units and 21.4% of 1,2-units.

The carbon–cobalt bond may be either a polarised covalent bond, a bridging bond, a π-allyl bond, etc. Without prejudging the nature of the bond, which requires special consideration, we can confine ourselves to the hypothetical scheme



to illustrate the chain-transfer reactions.

As an electron-acceptor agent, water solvates the cobalt atoms, increases its fractional positive charge, and strengthens the carbon–cobalt bond. The degree of solvation probably increases even after the concentration of water has reached a twentyfold excess over that of cobalt, which is necessary to stabilise the active centre and suppress chain-transfer reactions.

Other electron-acceptor compounds, such as aluminium trichloride, tin tetrachloride, and hydrogen chloride, also tend to strengthen the carbon–cobalt bond, but the concentration curves for the rate of polymerisation do not pass through a maximum, since these compounds are

devoid of the electron-donor properties which water possesses in some measure, as noted previously. The rate of polymerisation reaches a limit as their concentration increases.

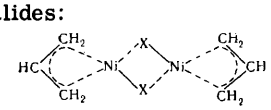
Strong electron-donor compounds (ethers, amines, tetrahydrofuran) tend to break down the active centres [58,59]. This may be supposed to be linked with a tendency to form ion-pairs, which are unstable in the case of the transition metals.

Weak electron donors, such as e.g. dialkyl sulphides, promote polarisation of the carbon–cobalt bond and, as might have been expected by analogy with the alkali metals, change the structure of the polymer units in the direction of forming 1,2-structures [60].

Thus the regularities which have been found determine the nature and the concentration of the initial active centres and the way in which they vary with the initial concentration of water, and correctly describe the changes in the molecular weight of the polymers formed by the polymerisation of butadiene in the presence of the complex system consisting of $CoPy_2Cl_2$, R_2AlCl, and H_2O.

2. Active Centres in the Polymerisation of Butadiene initiated by Nickel Complexes of the π-Allyl Type

The polymerisation of butadiene under the influence of nickel complexes of the π-allyl type now occupies an important place in researches aimed at elucidating the mechanism of polymerisation processes occurring in the presence of complex compounds of transition metals. A comprehensive study of the π-allyl type of complexes has led to several important conclusions on the dependence of their structure on the nature of the metal and the properties of the medium [61–63]. In particular, the structure of the bis-π-allylmetal halides has been established by the application of physical methods [64,65]. The diagrammatic representation of these complexes can be extended also to π-allylnickel halides:



(III)

where X = Cl, Br, I. However, no kinetic investigations were undertaken, which might have given important additional information on the nature of the active centres and their role in the polymerisation of butadiene. Lazutkin and Vashkevich [66] carried out the research necessary to obtain this information, their results being given later.

The pure complexes listed in Table 8 have been obtained by a new method of synthesis [67], and used as polymerisation catalysts. All operations in the preparation, purification, and dispensing of the starting materials and in polymerisation were conducted in a completely sealed apparatus,

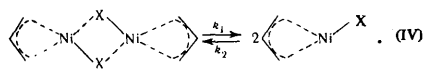
Table 8. Dependence of rate constant on nature of halogen and allyl group in nickel complexes.

Complex	Rate constant (65°C), $M^{-1/2}\,h^{-1}$	Activation energy, kcal mole^{-1}	Pre-exponential factor $10^{-10}A$
π-Allylnickel iodide	1.620	15.3	1.150
π-But-2-enylnickel iodide	1.170	15.2	0.710
π-Methylallylnickel iodide	1.320	15.0	0.590
π-Allylnickel bromide	0.130	15.2	0.078
π-But-2-enylnickel bromide	0.120	15.3	0.085
π-Allylnickel chloride	0.017	15.5	0.015
π-But-2-enylnickel chloride	0.010	—	—
π-Methylallylnickel chloride	0.017	15.5	0.015

which had first been conditioned under a high vacuum. It was found that, independently of the nature of the halogen or the substituents in the allyl group of the initial catalytic complex, the rate of polymerisation in benzene solution was given by

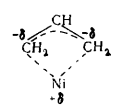
$$-\frac{d[M]}{dt} = k[Cat]^{1/2}[M].$$

This type of dependence of rate of polymerisation on the initial complex, which is unusual for complex systems, indicates that the active centres for chain growth are not dimeric molecules of the original complex but dissociation products:



(IV)

The activity of a monomeric nickel centre is due to its valency unsaturation together with its considerable solvation by benzene. The first stage in formation of an active centre may be addition of a monomer molecule as an adduct to the nickel atom, followed by its rearrangement into a polarised π-allyl bond.

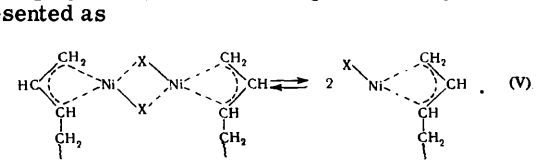


Dissociation of the initial complex is confirmed by the values of the Arrhenius parameters listed in Table 8. The total activation energy is surprisingly stable: for all the catalysts investigated, independently of the nature of the halogen and the allyl group, E_{act} = 15.0–15.5 kcal mole^{-1}. The pre-exponential factors also are practically independent of the nature of the substituent in the allyl group, but they increase substantially with the volume of the halogen atom, in the sequence Cl < Br < I. The increase in volume of the halogen atoms and the consequent steric hindrance constitute the main factor responsible for the increase in rate of polymerisation in the same sequence (Table 8).

All the facts which have been found fit the following kinetic scheme of polymerisation reactions:

1. $A_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2\mathring{A}$
2. $\mathring{A} + M \xrightarrow{k_{in}} \mathring{A}M$
3. $\mathring{A}M_n + M \xrightarrow{k_{gr}} \mathring{A}M_{n-1}$
4. $\mathring{A}M_n + \mathring{A}M_m \underset{k_4}{\overset{k_3}{\rightleftarrows}} M_nA_2M_m$

where A_2 is the initial complex, $\mathring{A}$ the monomeric active centre, M the monomer, and $M_nA_2M_m$ an inactive complex attached to polymer chains. The equilibrium system can be represented as



(V)

The dependence of the rate of polymerisation on the square root of the concentration of the initial complex, which is found to hold over a wide range of concentrations and at various temperatures, leads to two conclusions: (*a*) the equilibrium systems (IV) and (V) are governed by

similar parameters; and (*b*) in the equation for the equilibrium constant

$$K_{eq} = \frac{k_1}{k_2} = \frac{[A^*]^2}{[A_2]} = \frac{(2\alpha)^2[A]}{1-\alpha},$$

the degree of dissociation $\alpha \ll 1$, and then $[A^*] = K_{eq}^{\frac{1}{2}}[A_2]^{\frac{1}{2}}$.

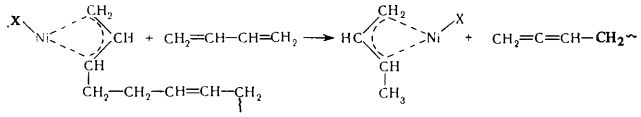
The rates of all the polymerisation processes investigated are given by the general equation

$$-\frac{d[M]}{dt} = K_{gr}K_{eq}^{1/2}[A_2]^{1/2}[M]$$

the changes in rate found with the chloride, bromide, and iodide complexes being determined mainly by variations in K_{eq} under the influence of the volume factor.

trans-1,4-Polybutadiene was always obtained in the presence of iodide and bromide complexes of nickel. The use of chloride complexes of nickel also yields polybutadiene in which *trans*-1,4-units predominate. Sometimes small quantities of *cis*-1,4-structures were also observed, but this cannot be attributed to a specific coordinating effect of the chlorine atoms in the complex. These structural deviations can rather be explained by impurities resulting from decomposition of the complex during prolonged polymerisation, which may last several days.

Chain-terminating reactions, which would have resulted in irreversible deactivation of the active centres, are absent from these processes. The mean molecular weights of the polymers formed are extremely low, varying over the range 10 000–35 000 depending on the condition and the nature of the nickel complexes. Chain-transfer reactions, which determine the molecular weight of the polybutadienes, probably occur as follows:



perhaps with intermediate formation of a hydride bond Ni–H.

Some Aspects of the Modification of Active Centres

The active centres of π-allylnickel halides are extremely sensitive to various substances—oxygen, iodine, Lewis acids, etc.—some of which break down the active centres, whereas others produce new centres possessing a different, sometimes enhanced, activity and, what is especially important, a different stereospecificity.

The system comprising $(NiC_3H_5Cl)_2$ and $TiCl_4$ is one of the large number of such examples[68]. When those substances are mixed in a heptane solution of butadiene, a precipitate of $(NiC_3H_5Cl)_2.TiCl_4$ is formed, and is a new catalyst. It contains all the nickel from the complex (the solution contains only titanium tetrachloride, and possesses no active properties). Polybutadiene of high molecular weight formed on the modified catalyst contains more than 90% of *cis*-1,4-units. This example illustrates an important fact of fairly wide validity: the addition of Lewis acids to solutions of π-allyl systems transfers the process of polymerisation to a heterogeneous phase, thereby changing the parameters of the reactive carbon–hydrogen bond not only owing to formation of a π-allyl complex differing in molecular structure but also in its phase constitution. This is especially significant in the consideration of the phenomena of stereospecificity, which is changed by additions to the reaction medium or the presence of substance of different type.

Another example of processes of this type is provided by results obtained in an investigation of the effect of added allyl halides on polymerisation systems containing π-allylnickel halides[69]. When various quantities of allyl bromide (ABr) are added to a benzene solution of butadiene and π-allylnickel bromide (π-ANiBr), the initial concentration of which in the mixture was the same (Fig. 7), the rate of polymerisation of the butadiene at first increases with increase in the initial concentration $[ABr]_0$, but after an optimum initial ratio is reached, in the present case $[\pi\text{-ANiBr}]_0/[ABr]_0 \simeq 0.5$, remains constant during some initial period (straight line *3*). It is interesting that with high $[ABr]_0$ concentrations the rate of polymerisation tends to a limit, and this occurs sooner the lower the initial ratio $[\pi\text{-ANiBr}]_0/[ABr]_0$ (curves *5* and *4*), which indicates complete decomposition of the initial catalyst (decolorisation of the solution).

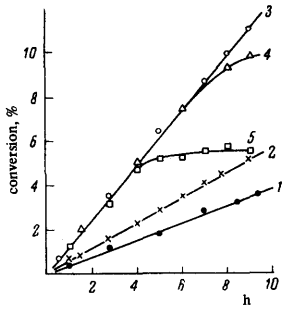
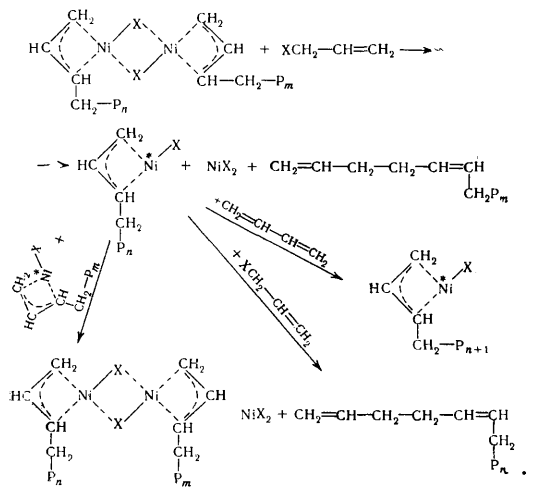


Figure 7. Polymerisation of 1.6 M butadiene in presence of 0.011 M π-allylnickel bromide at 49.3°C and allyl bromide concentrations (M) of: *1*) 0; *2*) 0.00187; *3*) 0.0242; *4*) 0.0512; *5*) 0.1624.

It is especially significant in these phenomena that decomposition of the initial complex π-ANiBr is accompanied by separation of NiX_2 as a highly disperse powder, which with the A_2 or A forms of the initial complex probably forms a new heterogeneous catalyst possessing enhanced total activity. The reactions which are involved in this process can be represented by the scheme



Similar phenomena take place on the addition of various amounts of allyl chloride (ACl) to the system containing π-ANiBr. The difference is that decomposition of the π-ANiBr complex occurs more slowly and with an induction period in the presence of ACl, and a higher $[\pi\text{-ANiBr}]_0/[\text{ACl}]_0$ ratio is required to produce a limiting state than when ABr is added. The total activity of the new complex on nickel chloride is increased several times.

The above results show that the polymerisation of butadiene in systems consisting of π-allylnickel halides and allyl halides involves complicated homogeneous and heterogeneous processes in which active centres of two different types take part, the nature and concentration of which depend on the initial ratio $[\pi\text{-ANiX}]_0/[\text{AX}]_0$ (where the X are halogen atoms which may be the same or different) and on the degree of conversion of the butadiene. The two types of active centres differ in stereospecificity: the homogeneous centres promote formation of *trans*-1,4-polybutadiene, whereas the heterogeneous centres result in preferential formation of *cis*-1,4-units of polybutadiene.

Both types of centre are present together in polymerisation processes, the relation between them being determined by the conditions mentioned above. For this reason the polybutadiene formed in systems containing π-allylnickel bromide have a mixed microstructure depending on the nature of the additions (see Table 9).

Table 9.

Addition	*cis*-1,4, %	*trans*-1,4, %	1,2, %
Allyl bromide	41—74	24—56	2—3
Allyl chloride	76	21	2—3

The facts discussed above provide further confirmation of the need to take into account heterogeneous reactions in the polymerisation of butadiene when considering problems of stereospecificity on the introduction of additives to systems containing the π-allylnickel halide type of complexes.

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Relative Strength of CH Acids

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The problem of the differentiating action of solvents on the relative strength of acids is examined from the point of view of the modern theory of acid-base equilibrium, according to which hydrocarbons and their derivatives behave under appropriate conditions as acids. Methods are described for determining the strength of such CH acids. The factors on which the differentiating effect of solvents depends are discussed. The most detailed consideration is given to the question—newly posed in the literature—of the possible causes of the change in the relative kinetic acidity of CH acids produced by solvents, which has been established by measuring the rate of the protophilic isotopic exchange of the hydrogen in them with bases. The bibliography contains 110 references.

CONTENTS

I. Introduction 845
II. Factors determining the differentiating effects of solvents 846
1. Correlation of thermodynamic and kinetic acidities 846
2. Differentiating action of solvents on thermodynamic acidity 846
3. Relative rates of steps and transition-state structures in protophilic isotopic exchange of hydrogen 847
III. Determination of strength of CH acids 848

I. INTRODUCTION

The essential nature of acid–base reactions and acid–base catalysis was explained by Brønsted's theory[1-5], which not only summarised many phenomena occurring in aqueous and non-aqueous solutions and gave a quantitative description of these phenomena but was also able to make predictions. In the course of time, however, facts accumulated which indicated that the theory was limited and imprecise[6,7]. Thus the discovery of the differentiating action of solvents on the relative strengths of acids and bases contradicted the theory. The mechanism of protolytic processes was found to be more complicated than was postulated by the theory, and substances which according to it were aprotic, i.e. incapable of acting as either acids or bases, could take part in such processes. It became obvious that the theory of acids and bases must be reexamined and refined, by changing the actual definitions of concepts. According to the new definitions[3,8] a *base* is an electron-donor reagent, which possesses affinity for a proton; an *acid* is an electron-acceptor reagent, whose hydrogen takes part in an equilibrium reaction with a base. An

acid combines with a base by means of a hydrogen bond or donates a proton to it. All substances containing hydrogen can under appropriate conditions react as acids. These include all organic compounds, among which are hydrocarbons[8,9]. They are termed carbo-acids or *CH acids*, since the hydrogen is combined with a carbon atom. Our knowledge of hydrocarbons, as of acids and their conjugate bases (carbanions), has greatly increased during recent years[6,10,11], while proof of the acidic function of hydrocarbons has now very greatly extended the acidity scale, which now covers about fifty pK_a units.

New methods were required for the quantitative assessment of the acidity of hydrocarbons, and it was proposed[6,9,14] to supplement methods of determining the equilibrium ionisation constants of the hydrocarbons, i.e. their thermodynamic acidity[12,13], by determining the kinetic acidity of hydrocarbons and their derivatives by measuring the rate constants for the isotopic exchange of hydrogen with strong bases. This method was intended for establishing the strength of very weak CH acids, right down to saturated hydrocarbons, and had the advantage of enabling a quantitative estimate to be made of the acidity of individual carbon–hydrogen bonds in organic molecules[15,16].

A prerequisite for use of the kinetic method to measure the acidities of organic substances is correlation between the rate constants and the ionisation constants of the acids. Correlation of this type was first expressed in the form of Brønsted's relation[17] (in logarithmic form $\lg k = \alpha \lg K + G$, where k is the rate constant, K is the equilibrium constant, and α and G are constants). The Brønsted relation is the prototype of the Hammett equation and its modifications. The physical meaning of all these equations reduces to a statement of the principle of the linearity of free energies[18-21].

An important conclusion of Brønsted's quantitative theory of acid–base equilibrium is that the relative strength of equally charged acids is independent of the solvent (S or M): i.e. $\lg (K_i/K_0)_S - \lg (K_i/K_0)_M$ is constant (where K_i is the ionisation constant of any acid and K_0 that of the standard acid). If values of $\Delta pK = pK_0 - pK_i$ in any two solvents are plotted along the coordinate axes, the points should lie on a common straight line passing through the origin at an angle of 45° to the horizontal axis. Actually, however, if the solvents differ in physical and chemical properties, the points for acids differing in structure lie on more than one straight line. This shows the differentiating effect of solvents on the relative strengths of acids as expressed by the value of ΔpK.

The present paper is concerned mainly with the differentiating action of solvents on the kinetic acidity of CH acids determined from the isotopic exchange of hydrogen. This question has been posed recently, and little work has yet been done on it. First it is necessary to consider briefly the factors on which depends the differentiating effect of solvents with respect to the strength of acids, and to indicate the methods which are available for determining the strengths of CH acids.

II. FACTORS DETERMINING THE DIFFERENTIATING EFFECTS OF SOLVENTS

1. Correlation of Thermodynamic and Kinetic Acidities

Arndt and Eistert[22] were the first to emphasise the necessity of introducing the concept of the proton lability of compounds, and to note that the dissociation constant K of an acid is by no means a simple function of the lability of the hydrogen it contains. In their opinion a parallelism between the dissociation constants of acids and the proton labilities of hydrogen in them, i.e. kinetic parameters, is possible only with compounds of similar structure. This was confirmed by Pearson and Dillon[23], who measured, from the rate of bromination, rates of ionisation in aqueous solution for a large number of CH acids containing one or more strongly polar groups (carbonyl, ethoxycarbonyl, nitrile, nitro, and sulpho). They compared the values of $\lg k$ and pK_a for the acids, the latter parameters being determined either by them or by other workers, e.g. potentiometrically or by some other method.

While a general correlation was observed between $\lg k$ and pK_a for a series of acids, large departures from it were found. The reasons for deviations from the Brønsted relation have been discussed in detail by Bell[5,24,25], Leffler, Grunwald[19,26,27], etc. The deviations are determined by the structure and the conditions of solvation of the initial substances, the transition states, and the reaction products. If the structure of the transition state on ionisation of the acid is close to the structure of its anion, the parameters tending to enhance the stability of the latter will stabilise also the transition state, and this should favour an increase both in the equilibrium constant and in the rate constant of ionisation; in this case correlation can be expected between $\lg k$ and pK_a.

Let us write the equation for the ionisation of CH acids by a base B in the form

$$\equiv C-H + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \equiv C^- + BH^+ \qquad (1)$$

where k_1 is the ionisation rate constant, k_{-1} is the rate constant of the reverse reaction (addition of the acid proton to the carbanion $\equiv C^-$), and $k_1/k_{-1} = K_a$ is the ionisation equilibrium constant.

Cram[10] notes that a linear correlation between rate constants and equilibrium constants of ionisation requires constancy of the rates of recombination of various carbanions with a proton having the same donor: in fact, if k_1 is constant, it follows that $k_1 = \text{const} \times K_a$.

2. Differentiating Action of Solvents on Thermodynamic Acidity

The reasons for the differentiating action of solvents on thermodynamic acidity have been discussed by Izmailov[7]. He shows that the dissociation of protolytes involves a series of equilibria—solvation of molecules and ions of the acids, ionic association—and deduces an equation for the dependence of the difference ΔpK_a between the dissociation constants of the acid in two solvents M and S on their properties, in particular their activities (a_M and a_S, the standard state being a vacuum), and on the energy of solvation of the molecules (A'_{mol}, A_{mol}) and the ions (A'_{ion}, A_{ion}) of the acid:

$$\Delta pK_a = \lg \frac{a_M}{a_S} + \lg \frac{K_{a(MH^+)}}{K_{a(SH^+)}} + \frac{\Sigma A'_{ion} - \Sigma A_{ion}}{2.3RT} - \frac{A'_{mol} - A_{mol}}{2.3RT} \qquad (2)$$

$K_{a(MH^+)}$ and $K_{a(SH^+)}$ being the thermodynamic acidities of the lyonium ions MH^+ and SH^+ respectively in M and S.

The first two terms in Eqn. (2) are the same independently of the structure of the acid. Hence the differentiating effect of solvents on the dissociation constants of acids depends on the relative solvation energies of the ions and molecules of the acid in the solvents. If the acids are similar in structure, the last two terms in Eqn. (2) differ

little in magnitude. This is not observed when acids differing in structure are compared in solvents of different types, and then a differentiating effect is observed.

Izmailov has also suggested that values of ΔpK_a should be measured by a method of single null activity coefficients γ_0, which represent the change in energy of a substance on passing from an infinitely dilute solution in any non-aqueous solvent to an infinitely dilute aqueous solution:

$$\Delta pK_a = 2 \lg \gamma_{0(ion)} - \lg \gamma_{0(mol)}. \quad (3)$$

The same equation has been deduced subsequently by Grunwald[28].

Differences in the energy of interaction of acid molecules differing in structure with solvents of different chemical types result from the formation of solvates differing in composition, stability, and polarity. According to Izmailov the solvates—not molecules of the acid itself—undergo ionisation. The differentiating action of solvents on the relative strengths of acids is due to differences in the solvation energy of ions and molecules by the solvent, differences in the solvation energy of the anions being especially important. This point was subsequently stressed also by Parker[29-31].

Equations (2) and (3) are thermodynamic in character, and do not reveal the nature of the forces responsible for solvation of the acid molecules and ions. Account must be taken[29] of the following parameters—proton affinity of the solvent molecule, its ability to form a hydrogen bond or other type of donor–acceptor interaction with the acid or with the anion, forces of electrostatic dipole–dipole and ion–dipole interaction, and also dispersion interaction between solvent molecules and acid anion—the last depending on the polarisability and the ionisation potentials of the solvent molecule and the anion, and on the radius of the latter. The electrostatic component of the solvation energy is a function of the dipole moments of acid and solvent molecules, the dielectric constant of the latter, and the ionic charge and radius (for further details see Refs. 7, 19, and 32–34).

3. Relative Rates of Steps and Transition-state Structures in Protophilic Isotopic Exchange of Hydrogen

Arndt and Eistert[22] pointed out that measurement of the rate of deuterium exchange could suitably be used for determining lability of hydrogen in organic compounds. They considered that signs of proton lability were absent with fluorene and triphenylmethane, for example, since these compounds exhibited no isotopic exchange of hydrogen with deuterioalcohol.

A kinetic method for the quantitative determination of the acid and basic properties of hydrocarbons follows from the concept of the protolytic nature of heterolytic isotopic exchange, in which hydrocarbons take part as acids or bases[35]. This idea arose and was justified during investigation of the isotopic exchange of hydrogen in hydrocarbons with non-aqueous solvents which are strong bases or acids[6].

In 1950 Shatenshtein and Vyrskii[14] proposed the use of liquid ammonia for determining the kinetic acidity of hydrocarbons. Because of the protophilic nature of ammonia and the high proton affinity of the amide ion, which catalyses exchange reactions in liquid ammonia, hydrogen can be exchanged for its isotopes even in saturated hydrocarbons, which are then reacting as very weak CH acids. This placed the kinetic method for determining the acidity of hydrocarbons on a practical course, and led to many analogous investigations in the USSR and abroad (see e.g. Tupitsyn and Zatsepina[36-38], Streitwieser[11,39-43], Schriesheim[44], Ebel[45], etc.).

It follows from subsection 1 that a condition for the kinetic method of determining the strength of CH acids to be applicable is a linear relation between their ionisation rate and equilibrium constants. And this in turn presupposes a direct relation between the measured rate constant of isotopic exchange and the ionisation rate constant of the CH acid involved in the exchange reaction.

The problem of the relation between the experimental rate constant of hydrogen exchange and the rate constants of its individual stages is closely linked with that of the structure of the transition state in the rate-determining stage of the isotopic exchange of hydrogen. Information on these questions is obtained by measuring the deuterium–tritium kinetic isotope effect (k.i.e.), i.e. the ratio of the rate constants for the exchange of deuterium and tritium respectively present in the same bonds with a carbon atom (k_D/k_T). The k.i.e. of reactions involving the protophilic exchange of hydrogen isotopes were first determined by Yakushin[46-49] in a series of studies in the Isotopic Reactions Laboratory of the Karpov Institute.

In exchange reactions with liquid ammonia (in absence of a catalyst and catalysed by potassamide) and also with aliphatic amines (methylamine and ethylamine) the ratio $(k_D/k_T)_{0-25\,°C}$ varied from 1.9 to 2.7 for different systems. Within these limits the ratio has a tendency to increase if the base becomes more protophilic or the reactivity of the CH acid increases.

Analysis of k.i.e. measurements combined with other data on protophilic substitutions of hydrogen (in particular on metallation reactions) has led to a two-stage mechanism[48,49]. The first stage consists in attack by the base B^- on the hydrogen atom combined with the carbon atom, the bond being stretched or in the limit ruptured with formation of the carbanion $\equiv C^-$:

$$\equiv C - D(T) + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \equiv C^- + D(T)B. \quad (4)\dagger$$

In the second stage a proton of the solvent molecule HB adds to the intermediate carbanion, to give a compound differing in isotopic composition:

$$\equiv C^- + HB \xrightarrow{k_2} \equiv CH + B^-. \quad (5)$$

The scheme does not include the gegenion (the metal cation), which is incorrect, since the gegenion can in principle be involved in the transition state.

If the bond with the hydrogen isotope is completely ruptured in the transition state, the k.i.e. value is calculated by means of the equation[50]

$$k_D/k_T = e^{N_0(h\nu_{C-D} - h\nu_{C-T})/2RT} \quad (6)$$

where k_D and k_T are the rate constants for exchange of protium by deuterium and by tritium, ν_{C-D} and ν_{C-T} are the C–D and C–T stretching frequencies, and $(k_D/k_T)_{25\,°C} = 2.6$. If deformation vibrations are also perturbed, $(k_D/k_T)_{25°C} = 3.2$.

It follows from theory[50-52] that maximum values of k.i.e. correspond to the case in which the reaction velocity is limited by the first stage (4), while its transition state has a linear three-centre structure $[C^{\delta-} \ldots D^{\delta+}(T) \ldots B^{\delta-}]^-$, the hydrogen isotope being located at the centre of symmetry

† The right-hand side of Eqn.(4) can also be written $\equiv C^- \ldots D(T)B$, to show that the carbanion is solvated, and then

$$\equiv C^- \ldots D(T)B \xrightarrow[HB]{k_2} \equiv CH + B^-$$

and the force constants of the C–D(T) and B–D(T) bonds being equivalent one to the other. According to Westheimer[51] disturbance of the symmetry of the linear three-centre transition state produces a decrease in k.i.e.

Bell[53] has shown that the degree of equivalence of the force constants of the bonds with the hydrogen atom in the transition state is measured by the difference in pK_a between the reactant CH acid and the conjugate acid of the reactant base. A symmetrical transition-state structure corresponds to $\Delta pK_a \simeq 0$; conversely, if ΔpK_a is large, the transition state is very unsymmetrical, and the ratio k_D/k_T differs little from unity.

The above experimental values of k_D/k_T, obtained from a study of exchange reactions with liquid ammonia and amines, are close to the theoretical maximum value. This enabled a two-stage mechanism to be considered, and the first stage of the reaction to be accepted as the limiting stage, while the transition state was almost symmetrical[46–49]. The results and the principal conclusions of this work[46–49] have been confirmed by Streitwieser[11,39–42], Tupitsyn[36–38], and Ebel and his coworkers[45].

For reactions occurring under steady-state conditions the concentration of the intermediate carbanion is constant, and the equation[10,36,54,55]

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (7)$$

links the experimental rate constant of the exchange reaction k with the rate constants of the stages k_1, k_{-1}, and k_2.

Let us suppose that the rate of the exchange reaction is limited by ionisation of the C–D(T) bond, while the intermediate carbanion is relatively stable. If $k_2 \gg k_{-1}$, we can neglect k_{-1} in the denominator of Eqn. (7). Hence $k = k_1$: i.e. the observed rate constant of the exchange reaction is equal to the rate constant for ionisation of the C–D(T) bond. In such case measurement of the kinetics of hydrogen exchange (in particular with liquid ammonia or with amines) adequately characterises the acidity associated with the given bond.

Kinetic studies of the protophilic isotopic exchange of hydrogen in C–H bonds with dimethyl sulphoxide catalysed by an alkali-metal t-butoxide has shown[56] substantial differences in the relative kinetic acidities of certain CH acids compared with those found from measurements in solutions in ammonia. A similar phenomenon was noted by Streitwieser[57] on comparing his kinetic measurements on exchange reactions in cyclohexylamine with Schriesheim's measurements[44] in dimethyl sulphoxide (for fuller details see below). Deuterium–tritium exchange with dimethyl sulphoxide gave[56,58–60] a value of k_D/k_T close to unity.

For deuterium–tritium exchange involving the methyl group of toluene in the dimethyl sulphoxide–potassium t-butoxide system Jones[61] has explained the low k.i.e. on the basis of Bell's conclusions[53], considering that, since the difference in pK_a between toluene and t-butyl alcohol is large ($\Delta pK_a \simeq 20$), the ionisation stage corresponds to an extremely unsymmetrical transition state. In this state the proton is far closer to the base (B^-) than to the benzyl anion (A^-): i.e. $[A^{\delta-} \ldots H^{\delta+} B^{\delta-}]^-$.

Cram[10,54,62] had earlier observed a low value of k.i.e. for racemisation catalysed by a t-butoxide in dimethyl sulphoxide. In his opinion, supported by Streitwieser[57,63] and by Schriesheim[60], the reason for the low k.i.e. is that the rate of the exchange reaction is limited by a stage—the second one (Eqn. 5)—which is insensitive to isotopic replacement of hydrogen in the CH acid. Its low rate may be due to the fact that t-butyl alcohol formed in the first stage (Eqn. 4) slowly diffuses away from the carbanion, which is again able to capture a heavy isotope of hydrogen: i.e. $k_2 \ll k_{-1}$‡. In such case the term k_2 in the denominator of Eqn. (7) can be neglected, so that $k = k_1 k_2 / k_{-1} = K k_2$. Thus there is no direct relation between the rate constants of the exchange reaction and of ionisation. If Cram's treatment is correct, the low value of k.i.e. is an indication that measurements of the rate of the exchange reaction in the given medium do not give a correct idea of the strength of the CH acid. We shall return to the discussion of this question again.

III. DETERMINATION OF STRENGTH OF CH ACIDS

The acidity of hydrocarbons was first measured by Conant and Wheland[12], and the acidity scale was improved and extended by McEwen[13]. In these studies a colorimetric method was used to examine metallation equilibria in benzene or ethereal solution

$$RH + R'M \rightleftarrows R'H + RM \qquad (8)$$

where RH and R'H are hydrocarbons, while RM and R'M are their metal derivatives. With pK_a for one substance taken as standard (on McEwen's scale methanol has $pK_a = 16$), the difference in pK_a is determined. Thus the scale depends on the standard adopted. This work, undertaken in the 1930s, has been continued only recently by Streitwieser and his coworkers[64,65], who have measured the equilibrium constants between lithium or caesium cyclohexylamide and hydrocarbons (mainly fluorene derivatives) in cyclohexylamine, with phenylfluorene having $pK_a = 18.49$ taken as standard

Several papers, mainly by American workers[62,66–72], have reported the use of an indicator method of determining Hammett's acidity function[73] for measuring the pK_a of CH acids. The function H_- represents the ability of a base to detach a proton from an electrically neutral acid HA. By definition

$$H_- = \lg \frac{a_{H^+} f_{A^-}}{f_{HA}} = pK_a + \lg \frac{A^-}{HA} \qquad (9)$$

where a_{H^+} is the proton activity, f_{HA} and f_A are the activity coefficients of the acid and its anion, and HA and A^- are their concentrations. In dilute aqueous solution the H_- scale is identical with the usual pH scale, which is its virtue (papers on the acidity function H_- have been reviewed[74]).

The function H_- has been determined for many systems containing bases (e.g. mixtures of dimethyl sulphoxide with water or alcohol, in which tetra-alkylammonium hydroxides, caustic alkalis, or alkoxides are dissolved—for reviews of several systems see Refs. 74–76).

Kuhn and his coworkers[77–80] have successfully used spectrophotometric measurements combined with H_- data to determine the pK_a of strongly acidic polycyclic ethylenic and other hydrocarbons containing a large number of fused rings (e.g. trisbiphenylenylvinylmethane, $pK_a = 6.2$).

Ritchie[32,33] has recently been able to develop a technique for the potentiometric determination of pK_a for CH acids using a glass electrode in non-aqueous solvents, in particular in dimethyl sulphoxide, this method being suitable for the determination of high values of pK_a (~ 30).

Apart from the above, other methods have been suggested for assessing the equilibrium acidities of hydrocarbons, e.g. by estimating the relative stability of carbanions,

‡ It is assumed[63] that the return stage (k_{-1}) is especially rapid if conversion of the carbanion into the hydrocarbon involves only slight changes in structure.

including those of saturated hydrocarbons, by measuring equilibria in which organometallic compounds are involved. Thus Applequist[81] recommended study of an equilibrium of type

$$RX + R'M \rightleftarrows RM + R'X \qquad (10)$$

(where X = I and M = Li) coupled with equilibrium (8). Dessy[82,83] has shown that a similar stability sequence of the carbanions is obtained by studying a series of exchange equilibria between organomercury and organomagnesium compounds

$$RMg + R'Hg \rightleftarrows RHg + R'Mg\,. \qquad (11)$$

In this paper we are unable to give results obtained by different workers or discuss the reasons for differences in the values of pK_a for the same hydrocarbons obtained by different methods and especially in different solvents, where the differentiating effect of the medium is exhibited[11,18,32,33,65,68]. Discrepancies between the values of pK_a depend both on the method of determination and the standard adopted and on the properties of the solvent, especially on the structure of the CH acids, and even on the nature of the gegenion. Work done before 1965 has been surveyed comprehensively in Cram's book[55], which has been translated into Russian[10].

The suitability of the kinetic method for determining the acidity of hydrocarbons from the rate of isotopic exchange of hydrogen first received a theoretical basis[14] from the existence of a correlation between the logarithm of the rate constant of deuterium exchange with liquid ammonia (the first numeral in the parentheses is the rate constant) and the pK_a value for the same hydrocarbon determined by McEwen[13] (the second numeral in parentheses)—indene (0.4, 21), fluorene (0.02, 25), triphenylmethane (2×10^{-7}, 33), diphenylmethane (7×10^{-9}, 35)—and similar papers have appeared since then.

Dessy[84] has compared McEwen's results[13] with the exchange rate constants (in a dimethylformamide–deuterium oxide–triethylamine mixture) of cyclopentadiene (0.011, 14–15), acetophenone (2.2×10^{-4}, 19), phenylacetylene (6.6×10^{-5}, 21), and fluorene (2.2×10^{-6}, 25). Streitwieser[11,85] has shown a linear relation between the relative rate constant measured in methanol with sodium methoxide as catalyst and the pK_a value which he determined in cyclohexylamine: 9-phenylfluorene (47, 18.5), benzo[*c*]fluorene (26.3, 19.4), benzo[*a*]fluorene (7.6, 20), 4,5-methylenefluorene (1.93, 22.6), fluorene (1, 22.9), and benzo[*b*]fluorene (0.60, 23.2).

A rather more indirect comparison establishes[86] a linear relation between the kinetic acidities of 9-substituted fluorenes determined in methanolic solution (45°C) and the dissociation constants of acetic acids having the same substituents (CH_3, CH_3CH_2, $C_6H_5CH_2$, CH_3OCH_2, CF_3).

The good correlation between the thermodynamic and the kinetic acidities of hydrocarbons induced Cram (Ref. 10, p. 28) to try to set up a single acidity scale for hydrocarbons, based both on equilibrium and on kinetic measurements made by McEwen[13], Streitwieser[11], Applequist[81], and Dessy[84] (including Wooding and Higginson's data[87] for acetylene). This scale is named after the authors as the MSAD scale. Cram[10] stresses that "subsequent work will undoubtedly lead to modification of this scale".

Mention may be made also of comparisons between the results of polarographic measurements and data on the stability of carbanions obtained by an independent method. Streitwieser[88] notes that only limited application can be made of the polarographic reduction of benzyl chlorides and polycyclic arenemethyl chlorides for determining the stability of carbanions.

Dessy[83] used the polarographic reduction of organomercury compounds for this purpose. Reutov, Beletskaya, and their coworkers[89,90] proposed a polarographic scale of CH acidity based on the correlation

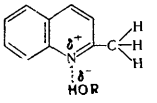
$$\alpha E_{1/2} = f(pK_a) \qquad (12)$$

where $E_{1/2}$ is the half-wave potential in the polarographic reduction of symmetrical organomercury compounds R_2Hg, α the electron transfer coefficient, and pK_a the ionisation equilibrium constant of the acid RH on the MSAD scale. Hence a correlation is observed between electrochemical kinetic data and the strengths of CH acids.

However, correlation is not always found between kinetic and thermodynamic values. The principal question in which we are interested in this paper is the differentiating effect on the relative kinetic acidity of CH acids determined by measuring the rates of isotopic exchange of hydrogen. Section II contains a general discussion of the factors which may govern the appearance of a differentiating effect.

We shall now show with actual examples that the change in the relative kinetic acidity can be caused both by specific solvation of the acids themselves, as a consequence of which the lability of the hydrogen varies, and by phenomena occurring during the reaction whose rate is used to measure the kinetic acidity.

For example, a comparison of the rates of isotopic exchange of hydrogen in certain hydrocarbons and nitrogen heterocycles with liquid ammonia and with alcohols showed[91] that the rate of exchange of hydrogen in a methyl group of the heterocycle is abnormally high in alcoholic solutions. Whereas the rate constant for the exchange of hydrogen in a methylene group in the hydrocarbon (indene, fluorene) with ammonia exceeds that with ethanol by factors of 10^7–10^8, hydrogen in the methyl group of quinaldine exchanges more rapidly with ethanol than with ammonia by a factor of 25. This is explained by specific solvation of the quinaldine molecule in alcoholic solution by formation of a hydrogen bond between the alcoholic hydroxyl and the nitrogen atom, which thus acquires a positive charge



Displacement of the electrons forming the methyl CH bonds towards the nitrogen facilitates protonation of these hydrogen atoms. The effect is stronger the more acidic the alcohol, and hence the higher the energy of the hydrogen bond: ethylene glycol (90, 547) > methanol (30, 50) > ethanol (20, 12) > propan-2-ol (7, 1) (the parentheses indicate the rate constants of the exchange reaction $10^7 k_{120°C}$ s^{-1} and the relative ionisation constants of the alcohol[92]).

An analogous differentiating effect is observed[93] on comparing the rates of deuterium exchange in the methyl group of quinaldine and in the methine group of triphenylmethane with ethylenediamine and aminoethanol. Owing to the more protophilic character of the former solvent, the hydrogen in triphenylmethane is exchanged five times as rapidly as in quinaldine, whereas with the latter solvent the hydrogen in quinaldine exchanges eight times as rapidly as in the hydrocarbon, because of the formation of a hydrogen bond between the alcoholic hydroxyl and the heterocyclic nitrogen atom.

In the above examples the differentiating action of the solvent on the kinetic acidity was due to the specific solvation in the ground state of molecules of CH acids distinguished from the others by their structure. Let us now

turn to examples which reveal the effect of catalytic systems in different solvents on kinetic acidities also determined by hydrogen exchange, where the differentiating effect depends on phenomena associated with the course of the reaction itself.

Mention has already been made (Section II, 3) of the very large differences in relative kinetic acidities which we have found[56] on comparing the kinetics of deuterium exchange with dimethyl sulphoxide (catalysed by potassium or lithium t-butoxide) and with liquid ammonia (catalysed by potassamide). Thus the rate constants for exchange with dimethyl sulphoxide of C–D bonds in the methyl group and in the ring of toluene were found to differ by factors of 10^6 instead of the 10^2 on exchange with ammonia[56].

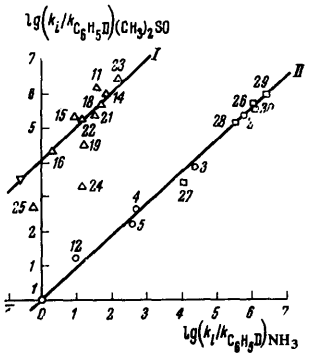
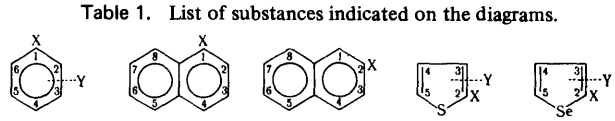


Figure 1. Comparison of kinetic acidities, determined in liquid ammonia with potassamide as catalyst, and in dimethyl sulphoxide with potassium t-butoxide as catalyst, for the exchange of deuterium in:
I) alkyl groups; II) the benzene ring and alkylthio-groups.

In Fig. 1[94] values of $\lg(k_i/k_{C_6H_5D})_{(CH_3)_2SO}$ are plotted against $\lg(k_i/k_{C_6H_5D})_{NH_3}$ for a series of CH acids (a key to the numbering of the compounds in Fig. 1 and the following diagrams will be found in Table 1). The points for the methyl groups in toluene, the xylene isomers, and the tolyl ethers (other than the *para*-isomers) and for the alkyl groups in alkylbenzenes lie on the straight line *I*, while those for benzene derivatives containing an *ortho*-deuterium atom are grouped about the straight line *II*. Points for alkylthio-groups attached to a benzene ring lie on the same line. The postulate that one reason for such a differentiating effect may be unequal conditions of solvation by the two solvents of transition states differing in structure is supported by the fact that the position of the deuterium atom in the toluene molecule, for example, does not affect the heat of solvation of the latter. Yet replacement of the solvent may have unequal effects on the heats of solvation of the transition states in the exchange of deuterium in the alkyl group and in the aromatic ring. Since the contribution of the heat of solvation of the transition state lowers the activation energy of the reaction *E*,[95] the unequal differences in the heats of solvation of the transition states by the two solvents will result in a differentiating action on the relative kinetic acidity of CH acids differing in structure. Tentative values of the activation parameters calculated from kinetic measurements (Ref. 6, p. 135) agree[96,97] in general with the above hypothesis.

The activation energies for exchange with ammonia catalysed by potassamide of hydrogen in the side-chain of alkylbenzenes (*14–16*)§ and in the ring of substituted benzene (*6–8*, *10*) have similar values of about 14.5–16.0 kcal mole^{-1}, and variations in the rates of the exchange reactions are associated with differences in the pre-exponential term. The activation energies for deuterium exchange in the dimethyl sulphoxide–potassium t-butoxide system are about 5–6 kcal mole^{-1} smaller for the substituents in alkylbenzenes than for the aromatic ring[94] (17.5–18.2 kcal mole^{-1} for compounds *14* and *15* compared with 23.0–24.5 kcal mole^{-1} for *3–5*)¶. Heats of solvation of benzene and toluene in dimethyl sulphoxide are the same within 0.25 kcal mole^{-1}.[99] On considering the origin of the differences in solvation energy of the transition states of deuterium exchange occurring in dimethyl sulphoxide and in ammonia, one is struck by the differing polarity of these solvents (Table 2, in which μ is the dipole moment and ϵ the dielectric constant). They differ also in their proton-donor properties, which are weakly developed in the CH bonds of dimethyl sulphoxide.

Table 1. List of substances indicated on the diagrams.



(I) (II) (III) (IV) (V)

No.	Formula	X	Y	No.	Formula	X	Y
1	I	D	H	*24*	I	CD_3	4-CH_3O
2	I	D	2-F	*25*	I	CD_3	4-$N(CH_3)_2$
3	I	D	2-C_6H_5O	*26*	I	SCD_3	H
4	I	D	2-CH_3O	*27*	I	SCD_3CH_3	H
5	I	D	2-CH_3S	*28*	I	SCD_3	2-CH_3O
6	I	D	2-C_6H_5	*29*	I	SCD_3	3-CH_3O
7	I	D	3-C_6H_5	*30*	I	SCD_3	4-CH_3
8	I	D	4-C_6H_5	*31*	IV	D	H
9	I	D	2-CH_3	*32*	IV	D	3-CH_3
10	I	D	3-CH_3	*33*	IV	D	4-CH_3
11	I	D	4-CH_3	*34*	IV	D	5-CH_3
12	II	D	H	*35*	IV	D	4-CH_3S
13	III	D	H	*36*	V	D	H
14	I	CD_3	H	*37*	V	D	3-CH_3
15	I	CD_2CH_3	H	*38*	V	D	5-CH_3
16	I	$CD(CH_3)_2$	H	*39*	II	CD_3	H
17	I	CD_3	2-CH_3	*40*	II	CD_3	4-CH_3
18	I	CD_3	3-CH_3	*41*	II	CD_3	5-CH_3
19	I	CD_3	4-CH_3	*42*	II	CD_3	8-CH_3
20	I	CD_3	4-*i*-C_3H_7	*43*	III	CD_3	H
21	I	CD_3	3,5-$(CH_3)_2$	*44*	III	CD_3	3-CH_3
22	I	CD_3	2-CH_3O	*45*	III	CD_3	6-CH_3
23	I	CD_3	3-CH_3O	*46*	III	CD_3	7-CH_3

47—$(C_6H_5)_3CD_3$ *48*—$CH_3CH_2CH_2CH{=}CH_2$

The transition states for the ionisation of CH acids are similar in structure to the carbanions. The dipole moment of the solvent, the effective charge, and the polarisability of the ions have a substantial effect on the ion–dipole and dispersion interaction energies. Molecules of proton-donor solvents are capable of forming a hydrogen bond with

§ Here and subsequently italic numerals relate to the numbering of compounds in Table 1.

¶ Still, tentative data suggest that a decrease in activation energy by 3–4 kcal mole^{-1} for the exchange of hydrogen in the alkylthio-groups[98] of methyl phenyl sulphide and ethyl phenyl sulphide compared with data for the aromatic ring in benzene derivatives applies to exchange both with liquid ammonia and with dimethyl sulphoxide. Thus this phenomenon requires further investigation.

the carbanion. Dimethyl sulphoxide can interact with a carbanion, since its sulphur atom is positively charged. Consequently new possibilities of solvation of the transition state appear when the solvent is changed. Nevertheless, their realisation depends on the structural peculiarities of the carbanion, especially those producing a particular degree of localisation of the negative charge on the carbon atom[94] (cf. Ref. 30). On these principles it becomes understandable that a differentiating effect should be developed when the acidities of CH acids (carbanions) differing in structure are compared in solvents which differ markedly in polarity and in proton-donor and other properties.

Table 2. Kinetic isotope effects of hydrogen exchange and polar properties of solvents.

Solvent	Catalyst	Temp., °C	k_D/k_T	μ, D	$\epsilon_{25°C}$
NH_3	KNH_2	0	2.7*	1.46	16.9
$C_6H_{11}NH_2$	$C_6H_{11}NHLi$	50	2.7	1.32	4.5(22°)
$(CH_3)_3COH$	$(CH_3)_3COK$	50	1.9*	1.66	12.3**
$(CH_3)_2SO$	$(CH_3)_3COK$	25	1.2	4.3***	46***
$(CH_3OCH_2)_2P(O)CH_3$	$(CH_3)_3COK$	25	1.3	3.6***	24.2***

* Determined by F.S.Yakushin.
** Mixture of 70 vol.% of t-butyl alcohol and 30 vol.% of 2,5,8-trioxanonane (dielectric constant of mixture ~10).
*** Determined in Yu.Ya.Fialkov's laboratory.

Let us now compare the kinetic acidities of a series of CH acids determined in dimethyl sulphoxide and in a mixture of t-butyl alcohol and 2,5,8-trioxanonane (diglyme), with an alkali-metal t-butoxide as catalyst. When

$$\lg (k_i/k_{(C_6H_5)_2CD_2})_{(CH_3)_2SO}$$

is plotted against

$$\lg (k_i/k_{(C_6H_5)_2CD_2})_{t\text{-}C_4H_9OH}$$

(Fig. 2), the points for five-membered heterocycles—thiophen[58,100], selenophen[101], and some of their derivatives containing a 2-deuterium atom—lie on a straight line (*I*), whereas the points for mono- and di-methylnaphthalenes[102], in which alkyl groups take part in the exchange reaction, are located near the straight line *II*. (Differentiation between the positions of the points for α- and β-isomers begins to show.) A common feature of the graphs in Figs. 1 and 2 is that points representing the acidity of C–H bonds in aromatic or heteroaromatic rings lie on one straight line, whereas points obtained from deuterium-exchange kinetics for methyl groups attached to the aromatic ring are on a second straight line. Furthermore, t-butyl alcohol, like liquid ammonia, differs from dimethyl sulphoxide in polar and proton-donor properties. Ammonia and t-butyl alcohol belong to one group of solvents, while dimethyl sulphoxide belongs to another group among those listed in Table 2. Cyclohexylamine is akin to ammonia both in chemical properties and in its dipole moment.

No differentiating effect is apparent when relative kinetic acidities are compared in solvents belonging to the same group in Table 2. In fact, if values of $\lg (k_i/k_{C_6H_5D})$ in ammonia[6,15] are plotted against those in cyclohexylamine[11,40–42], fifteen points for aromatic compounds lie on the straight line passing through the origin at an angle of 45° to the horizontal axis, independently of whether the exchangeable deuterium atom is present in the benzene ring or in an alkyl group (Fig. 3). Only the points for *o*-deuteriobiphenyl (*6*) and for cumene containing a deuterium atom in the methine group (*16*) lie away from the straight line. This is probably due to steric hindrance, for the cyclohexylamide ion and the cyclohexylamine molecule are larger than the amide ion and the ammonia molecule. It is noteworthy that the enthalpies of activation $\Delta H^{\neq}$ of the catalytic exchange reactions of benzene and of the methyl group in toluene with cyclohexylamine (13 and 15 kcal mole^{-1}),[42] as of the catalytic exchange with ammonia, are similar in magnitude and also differ little from that for the exchange of benzene with ammonia (15 kcal mole^{-1}).[103]

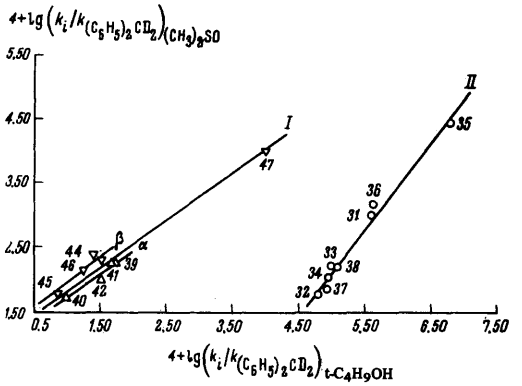


Figure 2. Comparison of kinetic acidities, determined in a mixture of t-butyl alcohol and 2,5,8-trioxanonane with potassium t-butoxide as catalyst, and in dimethyl sulphoxide with lithium butoxide as catalyst, for the exchange of deuterium in:
I) methyl groups; II) thiophen and selenophen rings.

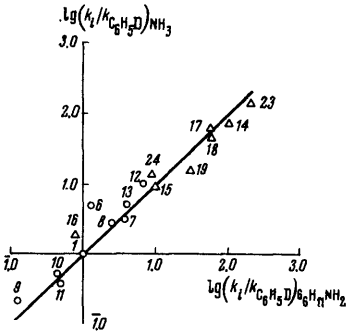


Figure 3. Comparison of kinetic acidities determined in cyclohexylamine with lithium cyclohexylamide as catlyst, and in liquid ammonia with potassamide as catalyst.

Fig. 4 compares the relative acidities $\lg (k_i/k_{C_6H_5CD_3})$ for a series of CH acids determined in catalytic systems with solvents—dimethyl sulphoxide[94] and methylbismethoxymethylphosphine oxide (medifos) $(CH_3OCH_2)_2PO.CH_3$ [104]—belonging to the second group in Table 2. In this case, too, the points for CH acids of different structural types, which in Fig. 1 are located on two straight lines, lie on one straight line. This also contains the point *24*, which in Fig. 1 occupied a position between the two straight lines.

The discussion and the facts lead to the conclusion that the differentiating action of the given solvents on the kinetic acidity of the CH acids listed in Table 1 depends on the structure and the solvation of the transition states formed during the protophilic isotopic exchange of hydrogen, at

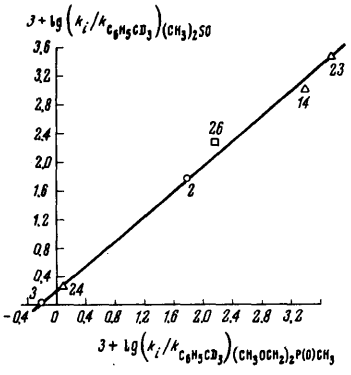


Figure 4. Comparison of kinetic acidities determined in methylbis-methoxymethylphosphine oxide and in dimethyl sulphoxide, with potassium t-butoxide as catalyst.

the ionisation stage of the CH acid. We shall not consider here the question of the structural features of the CH acids which predetermine the appearance of a differentiating effect in the catalytic systems assigned to different groups in Table 2.

Let us now consider the influence of solvents on the structure of the transition states and on the relative rates of the stages in the exchange reactions, which are shown in the k.i.e. value. Table 2 shows that the above division of solvents into two groups applies to a first approximation also to the ratios k_D/k_T, which have been determined[48,58,59] by measuring the rates of exchange of the heavy isotopes of hydrogen in the aliphatic bonds in toluene or diphenylmethane. Experiments with ammonia and cyclohexylamine have given k.i.e. values which are close to those calculated theoretically (Section II, 3). Hence it may be supposed that the stages of exchange reactions, the structure of the transition states, and their solvation are similar in these solvents, so that comparison of the relative kinetic acidities determined in them naturally reveals no differentiating effect, while measurements give a correct idea of the relative strength of the CH acids, since Brønsted's relation is observed. This is probably applicable also to the systems containing t-butyl alcohol which have been studied (Fig. 2), although this compound differs from ammonia and cyclohexylamine in its chemical properties, in that, being an OH acid, it is a stronger donor of protons. Differences in specific solvation are therefore possible, as we have seen, for example, in the solvation of heterocyclic molecules (p. 849). Alcohols readily solvate anions by hydrogen bonding.

Low k.i.e. values, close to unity, have been found[55,58-60] for exchange reactions in solvents belonging to the second group in Table 2 (dimethyl sulphoxide and methylbismethoxymethylphosphine oxide). As noted above (Section II, 3), there are two views (Jones[61] and Cram[10,54,62]) on the reason for the low k.i.e. in hydrogen exchange with dimethyl sulphoxide catalysed by an alkali-metal t-butoxide[59]. The former considers only the degree of symmetry of the transition state (within the framework of a linear three-centre model), whereas the latter view regards the second—not the first—stage in the exchange reaction as rate-determining.

With regard to the explanation put forward by Jones (cf. Ref. 59), account must undoubtedly be taken of the degree of symmetry of the transition states in reactions in which the C–H bond is broken. Actually, the transfer of a proton (deuteron) from 9-methylfluorene to the 5-methylphenanthren-4-yl carbanion[105] and from triphenylmethane to the dimsyl anion [anion derived from dimethyl sulphoxide][106] has k_H/k_D ratios of 4.2 and 4.7 respectively (or on conversion by means of Swain's equation[107] the k_D/k_T ratio is 1.9 and 2.0). The high k.i.e. value is consistent with the conclusion on the symmetry of the transition state, since, in conformity with Bell's principle, the difference in pK_a is close to zero (for the first reaction $\Delta pK_a = 19.7 - 20 \simeq 0$, whereas for the second reaction $\Delta pK_a = 29 - 33 = -4$[67,68,106]). For isotopic exchange between diphenylmethane and dimethyl sulphoxide catalysed by lithium t-butoxide, however, $(k_D/k_T)_{25°C} = 1.3 \pm 0.1$, although $\Delta pK_a = 30 - 28 = 2$,[67,68,106] and if the view of Jones is accepted, the higher k.i.e. value can be expected. It may be noted also that, for all the substances, differing in acidity, investigated by us[59], almost identical values of the ratio $(k_D/k_T)_{25°C}$ have been obtained (values indicated in parentheses): $\alpha(d)t$-diphenylmethane (1.3 ± 0.1), $2(d)t$-thiophen (1.3 ± 0.1), $2(d)t$-furan (1.5 ± 0.1), $(d)t$-methyl phenyl sulphide (1.2 ± 0.1), $\alpha(d)t$-toluene (1.2 ± 0.1), and o-$(d)t$-diphenyl ether (1.1 ± 0.1 measured at 50°C).

Nevertheless, a considerable k.i.e. ($k_H/k_D = 4.4$ at 55°C) is observed for the isomerisation of pent-1-ene catalysed by potassium t-butoxide in dimethyl sulphoxide[108], although on the MSAD scale (Ref. 10, p. 28) the values of pK_a for pentene and toluene are similar. In Schriesheim's opinion[108] proton transfer to the carbanion takes place intramolecularly in the isomerisation of an alkene, i.e. by a different mechanism from that operative in isotopic exchange.

The small kinetic effect observed in isotopic exchanges with dimethyl sulphoxide catalysed by alkali-metal t-butoxides is apparently due to some specific features of exchange reactions in these systems, as a consequence of which the rates of the reactions are limited at a stage which is unaffected by labelling the substance with heavy isotopes.

In this connection we note[59] that for the exchange reaction between the methylene groups in indene and fluorene, one of which is labelled with deuterium and tritium, the k_D/k_T ratio lies in the range 1.0–1.3. The reaction has been conducted[109] in ethylene glycol ethers, tetrahydrofuran, and dioxan with lithium t-butoxide as catalyst. The role of the solvent in the reaction is merely to solvate the cation and to polarise its bond with the anion: the solvent does not take part in the exchange reaction. The concentration of hydrocarbons in the solution is low, and the rate of the exchange reaction is probably limited at the stage of proton transfer from the C–H bond of the hydrocarbon to the carbanion, so that the k.i.e. is close to unity. We recall that solvents belonging to different groups in Table 2 differ in their proton-donor power. The first group, having high k.i.e., contains OH and NH acids, whereas the second group contains CH acids (dimethyl sulphoxide and the phosphine oxide), and it is for the latter solvents that the k.i.e. is small.

It must also be noted[59] that alkali-metal t-butoxides are strongly associated in ethereal solutions (this applies also to solutions in dimethyl sulphoxide, where the degree of association is lower[110]). It is possible that a two-stage scheme for the exchange reaction and a linear three-centre model for the transition state are unrealistic in the given case.

It must be borne in mind, of course, that the k.i.e. value in a given catalytic system may vary in some cases depending on the substance studied. Moreover, examples are known of a considerable change in k.i.e. for different bonds in the same substance undergoing exchange reactions in the same system[63].

Intensive research is now being conducted both on the theory of the kinetic isotope effect and on its determination in hydrogen exchanges occurring in different systems.

In Streitwieser's view[11,57] the differentiating effect observed on passing from cyclohexylamine to dimethyl sulphoxide is determined by the fact that in the latter solvent, depending on the structure of the carbanion, the ratio changes between the rate of diffusion from the carbanion of a molecule of the heavy alcohol formed from the alkoxide and the rate of return of the heavy hydrogen isotope from the alcohol to the carbanion. But different k.i.e. values can be expected for exchange reactions with dimethyl sulphoxide of those CH acids whose relative kinetic acidity changes unequally on change in the solvent (from cyclohexylamine or ammonia to dimethyl sulphoxide). However, the facts are not consistent with this conclusion, since practically identical values of k_D/k_T have been obtained[59] in dimethyl sulphoxide for several substances whose points lie on different straight lines in Fig. 1.

The discussion has shown that, if systems for which the k.i.e. values differ little from those calculated theoretically are used in determining kinetic acidity by the isotopic exchange of hydrogen, the measurements will be highly likely to give correct ideas of the relative strengths of CH acids (effects of specific solvation in the ground state of their molecules are disregarded). The applicability, for measurements of kinetic acidity, of systems in which the exchange reaction is characterised by a low k.i.e. is not such an unambiguous question. However, it would be wrong to conclude that catalytic systems such as those comprising dimethyl sulphoxide and an alkali-metal t-butoxide are completely unsuitable for such measurements[11,57]. Figs. 1 and 2 show that, within a group of structurally similar substances, a correlation has been established empirically between the relative acidities in systems belonging to different groups in Table 2†. However, there are deviations due to structural causes, e.g. for substances which contain, together with a *para*-methyl group, an electron-donor substituent (methyl, methoxyl, dimethylamino).

The results reported in this paper indicate that, in the present state of our knowledge, the problem of determining not only kinetic but also thermodynamic acidity is quite complicated owing to the variety of types of interaction between substances and solvents, as well as catalysts, in ground and transition states. Therefore the appearance of differentiating effects can by no means always be foreseen. This applies especially to the least studied, CH acids. Further, intensive research is required in this important field of theoretical organic chemistry, especially as the generalisations made will be extremely useful also for synthetic organic chemistry.

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Highly Disperse Aerosols

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The properties of highly disperse aerosols of particle size ⩽100 Å are described, together with methods for their production and investigation. This class of aerosols, which has not hitherto been investigated systematically, is of great interest for the theory of the formation of condensation aerosols, the problem of atmospheric pollution and the fight against it, rocket technology, etc.

Special attention is paid to the theory of the formation of highly disperse aerosols, their coagulation, the diffusion method for determining particle size, the preparation of highly disperse materials via the aerosol state, i.e. questions to which the Reviewers have paid special attention in their publications. The bibliography contains 48 references.

CONTENTS

1. Introduction 855
2. Formation of highly disperse aerosols 855
3. Determination of concentration and particle size of highly disperse aerosols 858
4. Rate of coagulation of highly disperse aerosols 861

1. INTRODUCTION

In the present paper the term highly disperse aerosols (h.d.a.) is used in the sense of aerodisperse systems having a particle radius of around 10–100 Å, i.e. a Knudsen number (ratio of mean free path of gas molecules to particle radius $Kn = \lambda/r$) exceeding unity at atmospheric pressure. The most important property of h.d.a. must be that processes involving the transfer of momentum, energy, and mass from the particles to the medium and *vice versa* are described by the formulae of the kinetic theory of gases: i.e. the particles can be regarded simply as large gas molecules. Therefore the resistance of the gaseous medium to movement of the particles, the rate of their evaporation and of heat transfer to them, and also the rate of thermophoresis of the particles are proportional to the square of their radius. Since the apparent mean free path λ' of the particles themselves is $660\rho^{1/2}$ and $220\rho^{1/2}$ Å for those of radius 10 and 100 Å respectively, where ρ is the density of the particles[1], the "aerosol Knudsen number" λ'/r also exceeds unity in h.d.a.; therefore their rate of coagulation is more or less accurately represented by the well known formula for the number of collisions between gas molecules with $r \simeq 10$ Å, and approximately with $r \simeq 100$ Å, the rate of coagulation increasing with increase in particle size.

The vapour pressure of h.d.a. particles appreciably exceeds the normal vapour pressure of the material of the particles (by several 10% for $r \simeq 100$ Å and several times for $r \simeq 10$ Å). The scattering of light by the particles obeys Rayleigh's law accurately, while the intensity of the scattered light is so small that it is impossible to determine the particle size and concentration by macroscopic methods, and the particles are invisible in the ultramicroscope.

The Brownian motion of h.d.a. particles is so intense, while their inertia and rate of sedimentation under the influence of gravity are so small, that the deposition of h.d.a. on walls, streamlined obstacles, etc. occurs solely as a consequence of diffusion. The charge acquired by the particles in a bipolarly ionised atmosphere does not exceed 1 unit, the percentage of charged particles falling with decrease in their size.

In all the respects mentioned here, h.d.a. differ markedly from aerosols of particle radius ⩾ 0.1 μm, which have hitherto been the main subject of aerosol investigations. It is noteworthy also that, in view of the above fact concerning the charges on h.d.a. particles, their electrical mobility exceeds 0.001 V cm s^{-2}; thus the charged portion of atmospheric h.d.a. belongs, in the terminology of aerophysicists, to "intermediate" atmospheric ions.

2. FORMATION OF HIGHLY DISPERSE AEROSOLS

Although aerosols obtained by mechanical pulverisation or electrostatic sputtering of liquids and solids quite often contain very fine as well as coarse particles, relatively few of the former are formed, and their presence has little effect on the properties of such aerosols. The present h.d.a., in which all or most of the particles have the size indicated above, can be produced only by condensation. This is usually "physical" condensation of the supersaturated vapour of substances† having a very low vapour pressure at room temperature, the supersaturation being produced by rapidly cooling the vapour. This category includes also aerosols obtained in the spark, corona, and arc discharges, and by the explosion of wires. If, however, the supersaturated vapour is formed by a gaseous chemical reaction, condensation of the vapour is complicated by the fact that reaction takes place both in the gas phase and on the surface of already formed particles, the latter process quite often being catalytic in character and preponderating considerably over the former. Mention must be made also of "molecular" aerosols formed in certain chemical processes. Kogan[2] has shown that, in the photochemical decomposition of $Fe(CO)_5$ vapour under certain conditions, aerosols are formed whose particles consist of individual $Fe_2(CO)_9$ molecules. This is essentially $Fe_2(CO)_9$ vapour in a state of immense supersaturation, but possessing all the typical properties of aerosols; in particular, its particles may cause the condensation of supersaturated vapours of high-boiling liquids, i.e. act as "molecular condensation nuclei". Another analogous example is provided by "atomic" aerosols formed by the radioactive disintegration of emanations[3].

† We are concerned here, of course, with spontaneous condensation, since the concentrations of the particles thus formed exceed by several orders of magnitude the possible concentration of foreign condensation nuclei, including gaseous ions.

The size of particles formed by physical condensation depends primarily on the relative rates of formation of condensation nuclei and of their growth by the condensation of vapour on them. It follows from the modern theory of spontaneous condensation that the former rate increases far more rapidly than does the latter with increase in supersaturation of the vapour: i.e. finer particles should be obtained with increase in supersaturation. In fact, with the same initial concentration of the vapour and temperature of the vapour–gas mixture, rapidly cooled to room temperature, the degree of dispersion of the resulting aerosol is greater the less volatile the substance, i.e. the greater the supersaturation. This is shown especially clearly with compounds belonging to the same homologous series: increase in molecular weight produces a regular increase in the degree of dispersion of the aerosol.

On the other hand, the time during which supersaturation is produced, e.g. the rate of cooling of a mixture of vapour and gas, is of very great importance here. With slow cooling the degree of supersaturation actually remains slight throughout, since vapour is continuously removed from the system by condensing on already formed particles, foreign condensation nuclei, and the walls of the vessel; therefore coarsely disperse aerosols are formed. The more rapidly the system is cooled, the greater the actual supersaturation and degree of dispersion of the resulting aerosol.

The theoretical conclusion that the particle size of the aerosol diminishes with increase in the degree of supersaturation appears to contradict the firmly established fact that coarser aerosols are obtained with increase in the initial concentration of the vapour while the rate of cooling is maintained. Some part is played here by the increased evolution of heat of condensation that accompanies increase in concentration of the vapour, which tends to slow down cooling. However, the main reason is probably linked with the secondary process of coagulation of the particles. With the immense particle concentrations which are produced at the extremely large supersaturations necessary for the formation of h.d.a., the rate of coagulation is extraordinarily high. Let us suppose that the size or number of particles in condensation aerosols can be determined 0.1 s after their formation. Then it follows from the theory of coagulation that, with any initial particle concentration exceeding 10^{12} cm^{-3}, the concentration has fallen to about the same value of 2×10^{10} cm^{-3} at the instant of examination. The mean mass of particles formed by coagulation will clearly be proportional to the initial concentration of the vapour. In particular, if the vapour pressure of the substance at the temperature of condensation is extremely small, it may be assumed that all collisions between vapour molecules, between them and molecular aggregates, and also between these aggregates will result in their sticking together ("avalanche" condensation). In this case the mean mass of the particle aggregates will also increase with increase in concentration of the vapour.

Coagulation is accompanied by other significant processes in the particles of h.d.a. Quite often particles, which are initially spherical in shape and amorphous in structure, are gradually converted into small crystals even at low temperatures[4,5]. This ordering process takes place far more rapidly at high temperatures, in particular when the particles are heated by the electron beam in an electron microscope. Still more important changes take place in the structure of aggregates. In general, the coagulation of aerosols involves the formation of extremely loose aggregates, in which the area of contact between the particles is negligible, so that they are extremely unstable. In the first stage of condensation, however, when the temperature of the system is still high, the atoms (or ions) in the particles are highly mobile, and intense sintering and recrystallisation of the particles takes place in the aggregates. Coarse particles are known to sinter at temperatures above the "Tammann point" ($\sim 0.6\,T_m$, where T_m is the melting point on the absolute temperature scale), whereas in very fine particles sintering is already possible at considerably lower temperatures[6]. Particles in the form of liquid droplets (and very fine droplets can be extremely strongly supercooled) coalesce on contact.

In most cases coagulation which has begun at a high temperature continues as the system is cooled, so that both dense coalesced, sintered, or recrystallised "primary" aggregates and loose "secondary" aggregates can be formed (aggregates in certain carbon blacks, for example, possess such a structure).

It must be stressed that there is a fundamental difference between aerosols comprising individual particles having radii of the order of 10–100 Å and aerosols containing more or less coarse aggregates of such particles. Only the former possess the characteristic properties of h.d.a. mentioned at the beginning of the paper, but aggregation of the particles is unavoidable on their sedimentation, and the powdered deposits thus obtained from uncoagulated and from coagulated aerosols (the latter containing only loose aggregates) are practically indistinguishable in properties. Coagulated h.d.a. are also of interest in view of the great practical value of such highly disperse powders.

Cooling of a mixture of vapour and gas, with the formation of condensation aerosols, can proceed uniformly throughout the volume of the mixture (when it is expanded adiabatically) or else under non-uniform conditions, when the temperature and the supersaturation differ at different points in the system (when the mixture of vapour and gas is mixed with a cold gas or when it is cooled externally). It is very difficult to produce in a Wilson chamber the high supersaturations necessary for formation of h.d.a.; this is far more easily achieved in supersonic nozzles[7,8]. Unfortunately, the h.d.a. formed in them vaporise extraordinarily rapidly, and they can be investigated only by indirect methods[9,10].

The most important method of obtaining h.d.a. is by mixing. This is achieved most simply by heating a weighed portion of the substance in a closed vessel[11–13], when mixing occurs by means of convection currents, and formation of the aerosol is almost uncontrollable. Furthermore, the resulting aerosol cloud is fairly slowly diluted with a neutral gas, and as a result a strongly coagulated and extremely polydisperse aerosol is obtained. In a similar method—the preparation of h.d.a. by exploding a wire[14,15]—mixing occurs far sooner, but in this case, too, the process of mixing is uncontrolled. A better method, enabling aerosols to be obtained which are more highly disperse and uniform in particle size, is mixing in a flow.

There are two ways—in a mixer and in free space—in which such mixing can be accomplished. In the former case the processes of mixing and condensation take place in the mixer itself, a considerable portion of the vapour condensing on the walls of the mixer. This lowers substantially the yield of aerosol, but on the other hand it helps to maintain a constant degree of supersaturation in the mixer, and hence a constant concentration and degree of dispersion of the resulting aerosol, and it diminishes the harmful effects of fluctuations in temperature and concentration of vapour in the mixture with air. This "buffering" action of mixers is especially apparent when for-

eign condensation nuclei are introduced into a cold gas flow with the aim of obtaining more monodisperse aerosols: at low concentrations of the nuclei almost all the vapour condenses on the walls, the actual degree of supersaturation in the mixer being practically independent of the rate of condensation in space, and as a consequence the size of the resulting particles is independent of their concentration[16].

When streams of gases are mixed in free space, the whole of the vapour is converted into an aerosol. There is no necessity for two streams to be present: a free turbulent stream of a hot mixture of vapour and gas, escaping from a nozzle into a cold, stationary gas, mixes with the latter sufficiently rapidly for h.d.a. to be formed. This method is preferable for the preparation of large quantities of h.d.a., but it has been less studied than has the preceding method.

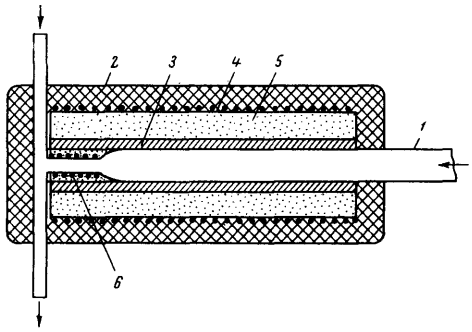

Figure 1. Generator for h.d.a.:
1) quartz tube; *2*) thermal insulation; *3*) steel tube; *4*) heating coil; *5*) ceramic tube; *6*) heating coil.

In the Laboratory for the Physics of Aerodisperse Systems at the Karpov Institute the formation of h.d.a. of sodium chloride has been studied by the method of mixing in a T-piece[17]. The generator illustrated in Fig. 1 was used. A quartz tube of diameter 20 mm, filled with ceramic rings coated with a layer of sodium chloride, was placed in an electric furnace operated with a stabilised voltage. The narrow part of the tube, which served as a superheater, was heated by a separate winding. In the steady state the temperature of the tube was maintained constant to 1 deg. The temperature profile along the axis of the tube shows that vaporisation of the salt took place under conditions of almost complete saturation with sodium chloride vapour of nitrogen flowing through the tube at a rate of 100–200 cm^3 min^{-1}. This is very significant, since work in which salt had been deposited as a thin layer on the surface of a nichrome coil had revealed a gradual fall in concentration of the vapour in the gas stream[18,19]; in this case the gas had obviously been far from saturated with the vapour, and recrystallisation of the salt on heating had caused a considerable decrease in the rate of evaporation.

The nitrogen and sodium chloride vapour leaving the tube were mixed in a T-piece with cold, filtered air flowing at a rate of 10–20 litres min^{-1}. In the absence of a superheater the vapour condensed completely on the walls of the mixer; with the superheater present, 90–99.9% of the vapour condensed on the walls depending on the experimental conditions. It was established by the method described on p. 860 that the h.d.a. obtained in this way were fairly monodisperse; the radius of the particles could vary from 7 to 50 Å, and the counted concentration from 10^2 to 10^7 cm^{-3}. The polydispersity of the h.d.a. increased appreciably at a radius of 50 Å. At the above concentrations the degree of coagulation of the h.d.a. was negligible. Both the size and the concentration of the particles increased with rise in the temperature of the furnace and with the rate of flow of nitrogen in it, i.e. with increase in the concentration of the h.d.a. by weight. A similar procedure was used to prepare h.d.a. from a series of alkali-metal halide salts.

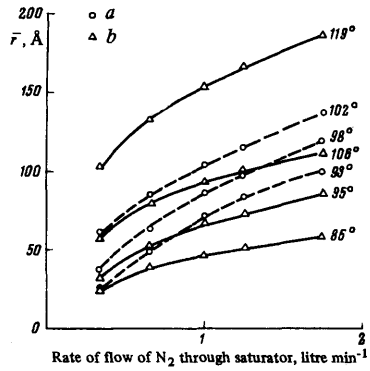

Figure 2. Dependence of mean particle size of dioctyl sebacate on conditions of operation of KUST apparatus, for air containing condensation nuclei (2×10^7 cm^{-3}) flowing at (litres min^{-1}): *a*) 11.0; *b*) 6.0. The temperature (°C) of the saturator are indicated on the curves.

Dioctyl sebacate h.d.a. have been prepared[20] by means of the KUST generator designed by Kogan and Burnasheva[16], in which the flows were mixed in a spray type of mixer: here a mixture of vapour and air escapes from a circular orifice, is mixed with a stream of cold air emerging from a concentric annular slit, and enters a diffuser. Condensation nuclei—the sodium chloride h.d.a. mentioned above, having $\bar{r} = 17$ Å—were used to obtain more monodisperse aerosols. In this way aerosols of dioctyl sebacate were prepared having $\bar{r}$ between 30 and 300 Å. Fig. 2 shows that the particle size increases with rise in the temperature at which the nitrogen is saturated by dioctyl sebacate vapour and with increase in the rate of flow of nitrogen through the saturator, as with the sodium chloride h.d.a. discussed above. In the present case, however, the degree of dispersion of the h.d.a. could be controlled also by varying the concentration of condensation nuclei: with increase in the latter above a certain limit (see above) the particle size understandably diminished.

By mixing gas flows in mixers, h.d.a. can very conveniently be obtained with controllable properties and a fairly high degree of monodispersity, but this method is unsuitable for the accurate study of the formation of aerosols by

physical condensation, since in the present case the process is greatly complicated by the condensation of vapour on the walls of the mixer. This disadvantage is absent when free streams are mixed, a method by which h.d.a. have been obtained from several substances in the Laboratory for the Physics of Aerodisperse Systems. Since there are no losses of material in this case, the concentration by weight of the resulting aerosols was considerably higher than in mixers, and the aerosols were strongly coagulated. The particle size in the aggregates was therefore determined from the specific surface of the deposited h.d.a.

The formation of h.d.a. has been studied in the greatest detail from molybdenum trioxide[21] and from silver[22]. The generator used differed from the apparatus illustrated in Fig. 1 by the absence of the T-piece: the narrow portion of the quartz tube (the superheater) terminated in a circular orifice, from which a stream of the hot mixture of vapour and air escaped into cold air, the molybdenum trioxide being placed in a boat in the furnace. Here vaporisation did not occur under saturated conditions, and the concentration of vapour in the mixture could be controlled both by the temperature of the boat and by the rate of flow over it. The aerosol formed in the turbulent stream was sucked without loss into an electrostatic precipitator, where it settled out. The specific surface of the deposit was determined by the BET method, and thence the mean particle radius was calculated.

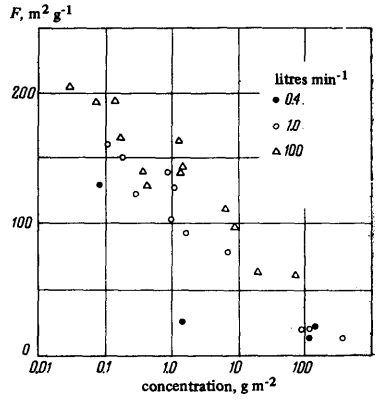

Figure 3. Dependence of specific surface of MoO_3 powders on concentration of vapour and rate of flow of air through producer (diameter of nozzle 2 mm, temperature at outlet from nozzle 820°C).

The content of molybdenum trioxide in the hot mixture of vapour and air is plotted as abscissa in Fig. 3, from which it is evident that the mean particle size in the aggregates increases with increase in concentration of the vapour. As already mentioned above, this is probably explained by coagulation of the aerosol at temperatures at which the particles in the aggregates coalesce or sinter. At low vapour concentrations the effect of coagulation is weaker, and the particle size is almost independent of concentration: the higher the latter, the stronger the influence of coagulation. The diminished particle size with increase in rate of flow is probably due to the accelerated dilution of the aerosol, so that it is less coagulated. In this case the effect of rate of flow will also clearly increase with vapour concentration.

Calculations on the formation of a silver aerosol, examination of electron micrographs of samples of the aerosol withdrawn at various stages in the process of formation, and investigation of the effect of heating on the specific surface of powders obtained by precipitating silver aerosols have shown that at vapour concentrations of 10^{14}–10^{16} mol. cm^{-3} coagulation plays a decisive part in producing the size distribution of the aerosol[22]. The final result is determined by the ability of the particles to coalesce and sinter on coagulation. As the aerosol cools, the coarse particles lose their ability to coalesce on collision, and merely sinter. This course of the process probably explains the spherical shape of the primary particles in certain aggregated aerosols of condensation origin, e.g. in carbon black aerosols. Other workers[13,23] have also concluded that coagulation, accompanied by coalescence of the particles, plays a decisive part in the formation of concentrated h.d.a.

A procedure analogous to that which has been described[21] has been used to obtain h.d.a. of bismuth molybdate, nickel chloride, and metallic silver. Allowing streams of argon containing the vapours of zinc, cadmium, bismuth, and tin(II) oxide to escape into air has yielded h.d.a. of the corresponding oxides and tin(IV) oxide having approximately the same particle size as with molybdenum trioxide, and in the case of tin dioxide $\bar{r} \simeq 15$ Å.

The preparation of h.d.a. by the decomposition of certain compounds in the plasma must also be included among processes in which aerosols are formed by the mixing of flows at different temperatures. As a consequence of the high temperatures reached in plasmas, the vapour formed by a chemical reaction probably becomes supersaturated only during cooling of the flow, and condensation is preceded by the chemical reaction. Examples of such processes are the preparation of carbon black by the decomposition of benzene vapour in the plasma, described by Sofronov[24], and the formation of nickel h.d.a.[25] by the decomposition of nickel pentacarbonyl.

3. DETERMINATION OF CONCENTRATION AND PARTICLE SIZE OF HIGHLY DISPERSE AEROSOLS

Only one method—enlarging the particles by condensing vapour on them—is in practice available for determining the number of particles in h.d.a. per unit volume. This method, which was proposed by Aitken as long ago as the nineteenth century, is based on the fact that condensation of a vapour on aerosol particles is possible at supersaturations which are insufficient for spontaneous condensation. Originally, water droplets formed by the adiabatic expansion of an aerosol containing water vapour were counted visually, but this method was too slow and laborious. At the present time, therefore, meteorologists employ photoelectric counters[26,27] to count "atmospheric condensation nuclei", these measuring the weakening or scattering of light by the aqueous mist formed on the adiabatic expansion of saturated air in the counter chamber. The counter is first calibrated by means of aerosols containing a known concentration of particles.

Use of the KUST apparatus mentioned above is considerably more convenient for laboratory investigations of h.d.a.[16] The test aerosol is mixed in a spray mixer with a gas flow containing the vapour of a high-boiling liquid, after which the concentration of droplets in the fairly monodisperse

fog formed is measured either visually or with a photoelectric particle counter. The great advantage of the KUST apparatus is that, at particle concentrations not exceeding 10^4 cm^{-3}, the size of the droplets formed by condensation no longer depends on the particle concentration. It is therefore sufficient to determine with a nephelometer the intensity of light scattered by the fog formed in the apparatus at one definite particle concentration in order to obtain the whole calibration graph (straight line). For relative nephelometric determinations of concentration, however, calibration is not required at all, since the nephelometer readings are proportional to the particle concentration.

To determine the absolute concentration of h.d.a. particles we had to ascertain the completeness of their "development" in the KUST[28]. For this purpose the particles were developed with an increasing degree of supersaturation of the vapour of the liquid developer (dibutyl phthalate). It was found that, in agreement with theory, there exists for each particle size a definite minimum supersaturation, at which all the particles are developed, further increase in the supersaturation (until spontaneous condensation begins) leading merely to enlargement of the fog droplets without change in their number. The minimum supersaturation necessary clearly increases with decrease in particle size. According to Kogan's hypothesis, liquids of extremely low vapour pressure, e.g. dioctyl sebacate, must be used to develop very fine particles; in this way he was able to develop "molecular" nuclei[2].

In view of the extremely large diffusion coefficient of particles having radii of around 10–30 Å, considerable losses of such particles from diffusion and thermophoresis to the walls were to be expected in the KUST apparatus. The design of the KUST mixer was therefore modified as shown in Fig. 4: the aerosol flows through the central orifice, while nitrogen containing superheated dibutyl phthalate vapour flows through the annular slit (the opposite to what occurs in the KUST apparatus). In this mixer the thermophoresis of particles preceding the mixing zone takes place from the walls towards the axis, and thus opposes the deposition of particles on the walls by diffusion.

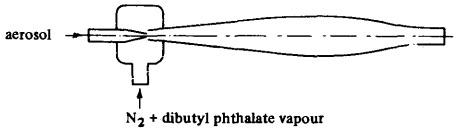

Figure 4. Mixer for developing aerosols.

Actually, the losses on the passage of an h.d.a. through a "blank" new mixer (i.e. in the absence of the vapour) were only 4% for $\bar{r}$ = 45 Å and 5.5% for $\bar{r}$ = 25 Å. Since these losses are caused by the diffusion of particles to the walls of the diffuser, the losses should be still smaller when the particles are enlarged by condensation. The fact that particles had sufficient time to be enlarged before they started to settle in the diffuser was established in special experiments.

In order to be able to utilise the above specific property of the KUST apparatus at concentrations exceeding 10^4 cm^{-3}, accurate dilution of h.d.a. was required. For this purpose an aerosol diluter was constructed[28], in which the deposition of h.d.a. by diffusion was insignificant, so that the dilution factor in such diluters varied little with particle size. The diluter was calibrated directly for each mean particle size at low h.d.a. concentrations under conditions of proportionality in the KUST apparatus, diluters having a dilution factor of around 10 being calibrated directly, while several diluters were connected in series for greater dilutions. The particle concentration in a developed diluted h.d.a. of droplet radius ~ 0.3 μm was determined by the classical ultramicroscopic method.

A large number of methods are theoretically available for determining particle size in h.d.a., but their applicability is greatly restricted in practice. Mention may be made of growing liquid h.d.a. particles in binary vapour mixtures[29,30], determining the size of sodium chloride particles by photometry of the flashes appearing on introduction of the particles into a hydrogen flame[31], and calculation of the radius from measurements of the capture coefficient for light ions[32].

Although a resolving power of the order of 5 Å has been achieved in modern electron microscopes, for several reasons no-one has yet been able to determine particle sizes less than 20–30 Å by this method, while for several substances the limit is considerably higher. In particular Megaw and Wiffen have found[33] that platinum and nickel particles of ~ 50 Å are either transparent to the electron beam or vaporise under its influence, and Young and Morrison[34] were unable to obtain micrographs of sodium chloride particles smaller than 200 Å.

Rich[35] suggested that, since the steady-state distribution of charges on aerosol particles in a bipolarly ionised atmosphere is given approximately by the Boltzmann formula and, as mentioned in the Introduction, h.d.a. particles are unable to carry more than one elementary charge, their size can be calculated from measurements of the percentage of charged particles. It must be borne in mind, however, that many hours are required for the charge on h.d.a. to reach a steady state under conditions of natural atmospheric ionisation, and therefore the aerosol must be subjected to extremely intense artificial ionisation—which is not usually done—for this method to be applied. Moreover, it is impossible by this method to obtain even a rough idea of the degree of polydispersity of the aerosol.

The well known method of determining the mobility of particles ("heavy" ions) in an electric field[36] permits the size distribution of only the charged particles to be measured. As the percentage of charged particles increases with increase in their size, this method will definitely overestimate particle size in the case of a polydisperse h.d.a.

Since the ability of particles to cause a vapour to condense depends not only on their size but also on their wettability, the presence of surface contamination, etc., the method of determining the particle size of h.d.a. from the critical degree of supersaturation of a vapour cannot give any reliable results[37].

An extremely simple and convenient method for determining the degree of dispersion of aerosols is based on measurement of the specific surface of a deposited aerosol from adsorption isotherms, but this method does not enable individual particles to be distinguished from aggregates, and it gives the mean size of primary particles and primary (i.e. coalesced or sintered) aggregates; on the other hand, in the case of h.d.a. which are highly concentrated by weight, in which a high degree of aggregation is unavoidable, only this method and electron microscopy are applicable in practice.

In several cases the Debye–Scherrer X-ray method, based on the broadening of the lines in the powder diagrams of very fine crystalline particles, proves to be extremely useful. It must only be remembered that the particles may consist of several crystallites, and results given by the Debye–Scherrer method relate to the dimensions of these latter. On the other hand, h.d.a. particles are quite often amorphous, and this can be established only by X-ray examination.

The most convenient way of measuring the particle size of h.d.a. is probably the diffusion method, based on passage of the h.d.a. through a circular or plane-parallel channel (or a "diffusion battery" comprising several channels) with measurement of the breakthrough (the ratio of the h.d.a. concentration at the outlet to that at the inlet to the channel). By means of the formulae deduced by Townsend and subsequently refined[38] the diffusion coefficient of the particles and hence their size can be calculated from the breakthrough value. Calculation shows that the charge on the h.d.a. particles has practically no effect on their breakthrough[39,40]. For a long time this method was employed only to determine mean particle size, but during recent years a series of attempts has been made to use it to determine the particle size distribution. The greatest theoretical interest is presented by Twomey's work[41], which showed that the distribution curve can be found from the curve of breakthrough against length of channel or rate of flow by means of the inverse Laplace transformation. Unfortunately, relatively small, unavoidable errors in the measurement of breakthrough lead to very large errors in the distribution function calculated in this way, and Twomey's method is probably applicable only to extremely polydisperse, e.g. atmospheric, aerosols. A method proposed by Pollak and Metnieks[42] enables the particles in an aerosol to be divided only into a small number of fractions.

The Laboratory for the Physics of Aerodisperse Systems uses a method based on the hypothesis that the particle size distribution in an aerosol is a logarithmic normal distribution[17,43]. This distribution is in fact observed more or less accurately in most aerosols, of both condensation and dispersion types. A computer has been used to calculate breakthrough curves through the channel as a function of the parameter $\mu = Dl/h^2\bar{u}$ (where $\bar{u}$ is the mean rate of flow in the channel, l its length, D the diffusion coefficient, and h the radius of a cylindrical channel or the half-width of a plane-parallel channel) for h.d.a. having different mean geometrical radii r_g and geometric standard deviation β_g. The breakthrough having been measured for a series of values of μ, the curve is selected which best fits the experimental points, and hence r_g and β_g are found. Then the Einstein–Millikan formula

$$D = kT[1 + A(\lambda/r) + (\lambda/r)\exp(-\gamma r/\lambda)]/6\pi\eta r \qquad (1)$$

(where η is the viscosity of the gas, λ is the mean free path of the gas molecules, and A, B, and γ are coefficients whose values are known for a series of substances) is used to calculate the size distribution curve for the particles regarded as spherical. For $r \leq 50$ Å, we can now use the simpler formula of gas kinetics

$$D = kTQ\lambda/6\pi r^2\eta \qquad (2)$$

in which we put $Q = 1.15$.

The apparatus used in the Laboratory for the Physics of Aerodisperse Systems to determine the particle size of h.d.a. by the diffusion method[17] is shown diagrammatically in Fig. 5. The aerosol leaves the producer A, is cooled to room temperature in the condenser B, and passes through the diluter D, where its concentration is brought to $\sim 10^4$ cm^{-3}. To obtain the desired rate of flow through the diffusion battery G (measured by means of the flowmeter F), part of the aerosol has been allowed to escape through E. After the battery the h.d.a. enters the KUST apparatus M and the nephelometer L. If the concentration of aerosol in the battery is to be diminished, part of it is passed through the filter K, and is mixed with the aerosol in such a way that the rate of flow in the KUST apparatus remains constant. To investigate h.d.a. having a mean particle radius of 25 Å, a set of diffusion batteries, differing in length and comprising eight cylindrical channels, is used. Over the mean particle radius range 25–100 Å, a set of sixty-channel batteries is used. For the investigation of aerosols of lower degree of dispersion, use can advantageously be made of measurement of deposition in plane-parallel slits.

With h.d.a. of particle radius ~ 10 Å, a difficulty is met when the diffusion method is used, in that all calculations for diffusion precipitation in channels start from the assumption that a parabolic flow profile has been formed in

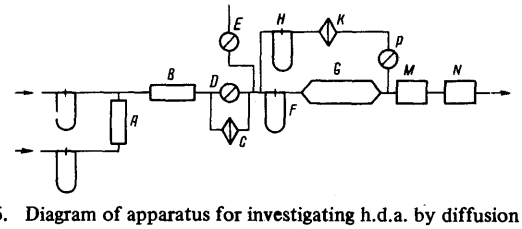

Figure 5. Diagram of apparatus for investigating h.d.a. by diffusion method.

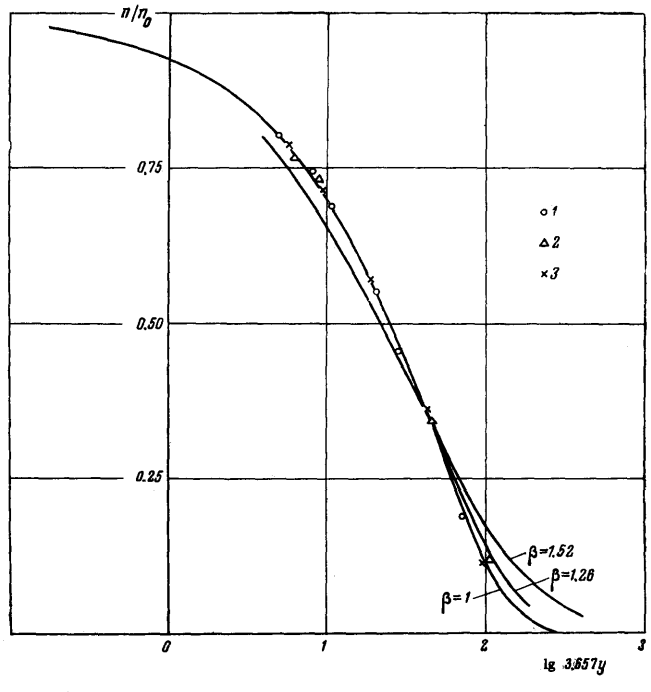

Figure 6. Theoretical curves and experimental values of breakthrough of sodium chloride aerosol through a battery of circular channels for different values of $\bar{r}$ (Å):
1) 11.8; *2*) 9.7; *3*) 7.0.

them. Naturally, the channels contain an entry section, deposition in which is significantly greater than calculated by the above method. It is very difficult to calculate theoretically the errors arising in this way, and the appropriate correction has been found experimentally.

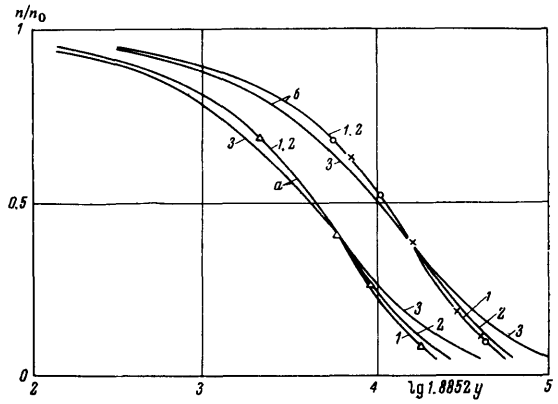

Figure 7. Diffusion breakthrough of dioctyl sebacate aerosols through an annular slit for different values of $\bar{r}$ (Å):
a) 100; *b*) 160; and of β_g: *1*) 1.0; *2*) 1.26; *3*) 1.54.

Fig. 6 illustrates the results of the measurements of particle size in sodium chloride h.d.a. mentioned in Section 2. The full lines have been calculated for different values of β_g (above the point of intersection the curves for $\beta_g = 1$ and 1.26 practically coincide). As is evident from Fig. 6, β_g is in any case less than 1.26 for the aerosols investigated. Fig. 7 shows analogous results for dioctyl sebacate h.d.a.[20] having a mean radius of 100 Å.

We thus see that the mean particle size of h.d.a. can be fairly accurately determined by the diffusion method, and the dispersion of sizes less accurately.

4. RATE OF COAGULATION OF HIGHLY DISPERSE AEROSOLS

As stated in the Introduction, the coagulation of h.d.a. takes place by a gas-kinetic mechanism: i.e. the coagulation constant K is given by the formula for the number of collisions between gas molecules. Nevertheless, a fairly substantial correction must be made to this formula for particles of radius 100 Å, i.e. for the upper limit which we adopted for the size of h.d.a. particles. No reliable experimental data on the magnitude of the coagulation constant of h.d.a. had been obtained until recently.

The chief difficulty in measuring the rate of coagulation of h.d.a. is the considerable loss of particles on the walls of the apparatus and connections due to the high diffusion coefficient of h.d.a. particles, which renders inapplicable the classical method, determination of the particle concentration in samples withdrawn from the chamber at intervals. Therefore a flow method was used in the Laboratory for the Physics of Aerodisperse Systems: an aerosol having a previously measured large counter concentration was passed with streamline motion through a vertical tube of capacity 2 litres.[28] Nephelometric measurements were made of the ratio of the concentrations entering and leaving the tube and of the mean residence time of the h.d.a. in the tube. In a separate experiment a greatly diluted non-coagulating h.d.a. was passed through the tube, and the correction for the diffusion losses of particles was determined.

The rate of flow varied from 10 to 17 litres min^{-1}, and the Reynolds number from 300 to 500. In order to diminish diffusion losses, the central portion of the flow (about half the total flow) was withdrawn isokinetically from the tube. It was established by special experiments that transverse mixing by convection did not occur in the cylindrical part of the tubes. Nevertheless, 6–14% of the particles, depending on the particle size and the rate of flow, were lost by diffusion in the tubes.

When the flow was made visible by means of an optically dense aerosol, appreciable circulation was observed in the diffusers, and most of the loss undoubtedly occurred in them. Since their volume was considerably less than that of the cylindrical portion of the tubes, it could be assumed that these losses preceded coagulation of the aerosols. The degree of coagulation (the ratio of the counted concentrations before and after coagulation) was therefore calculated by means of the formula $\epsilon = (n_1/n_2)/(n_1'/n_2')$, where n_1'/n_2' is the concentration ratio for the diluted (non-coagulating) aerosol, and n_1/n_2 the ratio for the undiluted (coagulating) aerosol.

To determine the residence time of the aerosol in the tube, which is practically identical with the coagulation time, pure air was first passed through the tube, and then after a certain time a coarse mist (or conversely), and the concentration of the mist emerging from the tube was determined as a function of time by means of a nephelometer. The mean residence time of the h.d.a. in the tube was calculated from the elution curves obtained.

These experiments gave mean values of K of 13.4×10^{-4} and 15.0×10^{-10} cm^3 s^{-1} for mean radii $\bar{r}$ of 25 and 45 Å respectively, the corresponding standard deviations being 11.5% and 12.5%. A detailed analysis of the sources of error in these measurements showed that the total square error in the value of K is 11.0%.

Comparison of experimental and theoretical values of K showed the latter to be considerably smaller (4.82 and 6.45×10^{-10} cm^3 s^{-1}). Such a large discrepancy is probably due to the effect of intermolecular forces on the coagulation constant. The "time lag effect" in intermolecular forces is known to diminish their magnitude at distances exceeding 200 Å so much that these forces play no appreciable part in the coagulation of coarse aerosols. With particles of radius 25 and 45 Å, on the other hand, the time lag effect can be neglected, and the potential for the intermolecular forces between two spherical particles can be calculated by means of Hamaker's[44] formula

$$V(\rho) = \frac{A}{6}\left[\frac{2r^2}{\rho^2} + \frac{2r^2}{\rho^2 - 4r^2} + \ln\left(1 - \frac{4r^2}{\rho^2}\right)\right] \qquad (3)$$

where ρ is the distance between the centres of the particles and $A = \pi q^2 \beta/6$, in which q is the number of molecules per unit volume of the substance and β is London's constant. The latter was determined for sodium chloride by Mayer from its ultraviolet absorption bands[45], and found to be $\beta = 1.8 \times 10^{-56}$ erg $Å^6$. The theory of collisions between gas molecules when forces of attraction operate between them shows that with this value of β the molecular forces increase the number of collisions, and hence the coagulation constant, by a factor of 2.19, independently of the particle size. From this we obtain theoretical values of 10.5 and 14.1×10^{-10} cm^3 s^{-1} for K, which show considerably

better agreement with the experimental results. The remaining discrepancy may be due to some polydispersity of the aerosols, which appreciably increases their rate of coagulation.

A coagulation constant of 13.4×10^{-10} cm^3 s^{-1} has been obtained[46] for dioctyl sebacate aerosols having $\bar{r} = 100$ Å. The gas-kinetic formula disregarding intermolecular forces gives $K = 10.5 \times 10^{-10}$ cm^3 s^{-1}, but this formula is not applicable in this case. A formula deduced by one of the present Reviewers[47], which is applicable at small Knudsen aerosol numbers exceeding unity, gives $K = 12.0 \times 10^{-10}$ cm^3 s^{-1} (without taking into account molecular forces).

It is curious that, for the coagulation of h.d.a., many authors use Smolukhovskii's formula even at the present time, substituting in it Eqn. (1) for the diffusion constant, and obtain excessively large values for the coagulation constant[48]. Without making due allowance for diffusion losses, some of these authors obtain the same excessively large experimental values for the coagulation constant.

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The systematic study of highly disperse aerosols began only quite recently, and it is still early to speak of their application to physics and technology, but we can already point to a number of problems in whose solution h.d.a. may prove useful. For the theory of the condensation of a vapour it would be extremely important to establish the relation between the critical supersaturation and the particle size of h.d.a., and for meteorology to determine the size of solution droplets formed in h.d.a. from hygroscopic substances at a given atmospheric humidity. By measuring the rate of vaporisation of h.d.a. particles (from the increase in their diffusion coefficient) of substances having a sufficiently low vapour pressure, we can determine the latter for particles which are so fine that the Kelvin equation cannot be applied. It may be hoped that refinement of the technique for measuring the coagulation constant of h.d.a. will yield a new method for evaluating intermolecular forces.

The finely divided powders obtained when h.d.a. settle out are also of great interest. In view of their immense specific surface and the structural disorder of the particles, they probably possess great chemical activity, and may find use as catalysts. Interesting data in the investigation of various physical phenomena depending on particle size—magnetic properties, the Mössbauer effect, etc.—can be obtained by the use of such powders. By measuring the heat of dissolution of finely divided powders of certain salts, it has been possible to determine their specific surface energy. It may prove possible to obtain high-quality diffusion membranes by sintering finely divided metal powders.

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Formation of Donor-Acceptor Complexes

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Results are summarised for the main principles governing the formation of complexes of type σn, νn (of halogens, metal halides, and organometallic compounds with various amines, ethers, and sulphides). The dipole moments and the heats of formation of the complexes are examined as the most important parameters characterising the properties of donor-acceptor bonds. Methods of determining these parameters are analysed.
Special attention is paid to the character of the relation between the degree of charge transfer and the energy of intermolecular bonds.
Two aspects of the problem of the donor properties of amines, ethers, and sulphides—the effect of molecular structure on the donor properties of the heteroatom, and the conditions for overlap of orbitals involved in the formation of donor-acceptor bonds—are discussed.
A method for determining the energy of p_π-conjugation in aromatic compounds containing a heteroatom is briefly described.
The list of references contains 81 items.

CONTENTS

1. Introduction 863
2. Determination of dipole moments and heats of formation of molecular compounds 864
3. Structure of complexes of donor-acceptor type 865
4. Degree of charge transfer and stability of intermolecular bonds 867
5. Donor properties of amines, ethers, and sulphides 869
6. Determination of energy of p_π-conjugation in aromatic compounds containing a heteroatom by the method of complex formation 871

1. INTRODUCTION

The nature of the intermolecular bonds in compounds of donor–acceptor type has remained a matter of controversy. The interpretation of π-complexes as charge-transfer complexes[1] is open to doubt[2]. It is supposed that the relatively low bond energies in π-complexes may be due to van der Waals forces, dipole–dipole interaction, and polarisation forces, and are not associated with charge transfer. A large number of molecular compounds are known whose formation is accompanied by a considerable change in dipole moments, which indicates a displacement of electron density or a transfer of charge from one component to the other on complex formation.

Within the very wide range of properties of intermolecular bonds it is impossible to draw a sharp distinction between strong and weak complexes. It is probable that the formation of intermolecular bonds between two valency-saturated molecules involves the maximum development of all possible forces—including polarisation, dipole–dipole, and van der Waals forces—and use is also made of the valency expansion possibilities of atoms and molecules responsible for donor–acceptor interaction. Each factor makes its contribution to the overall effect of formation of a molecular compound. Specific properties of molecular compounds and of intermolecular bonds will appear depending on how large a particular contribution is, the latter being determined by the composition and structure of the initial molecules.

The present Review will survey molecular compounds in which the transfer of charge predominates over other forces: i.e. compounds will be examined to which there is every justification for applying the term "charge-transfer complexes". Complexes formed by metal halides with various amines, ethers, sulphides, and also with certain aromatic compounds will be considered. It is supposed that the formation of intermolecular bonds in compounds of this type is accomplished mainly by partial transfer of an electron (or displacement of electron density) from the donor molecule to the acceptor molecule.

A necessary condition for the formation of an additional bond between two valency-saturated molecules is the presence of an occupied orbital of sufficiently high energy in the donor molecule and the presence of a sufficiently low unoccupied molecular orbital in the acceptor molecule. If electron transfer from a high filled orbital of one molecule to a lower free orbital of another is energetically favourable, a donor–acceptor bond is formed.

From the point of view of the theory of localised pairs, such an intermolecular bond is similar to an ordinary chemical bond produced by a pair of electrons in the field of two nuclei. The fundamental difference is that each atom supplies one electron to the formation of an ordinary chemical bond, whereas here one molecule—the donor—supplies the pair of electrons, while the second molecule—the acceptor—provides the vacant molecular orbital. Consequently, the properties of intermolecular bonds have many features in common with those of ordinary chemical bonds, as will be shown later, but they also exhibit their own specific characteristics.

Thus intermolecular bonds are formed by interaction between quite definite molecular orbitals in electron-donor and electron-acceptor molecules. The properties and the stereochemistry of such complexes will depend to a considerable extent on which orbitals are involved in forming the bond.

The existing classification[3] of molecular compounds of donor–acceptor type is based on the type of orbitals involved in bond formation. According to this, all molecules capable of developing donor properties, i.e. of donating an electron on interaction with other molecules, can be divided by means of the structural criterion into three groups—n, σ, and π—in the first of which the energetically highest orbital is the lone pair of n-electrons of the heteroatom (R_2O, R_2S, R_3N, etc.), in the second the pair of electrons of the σ-bond (R–Hal), and in the third a pair of π-

electrons of unsaturated and aromatic compounds having a sufficiently low ionisation potential.

Acceptor molecules can also be divided structurally into three groups—v, σ, and π—the lowest molecular orbital in the first being the vacant v-valency orbital of the metal atom (metal halides, certain organometallic compounds), in the second the non-bonding σ-orbital (I_2, ICl, Br_2, etc.), and in the third the system of π-bonds (aromatic and unsaturated compounds containing electron-acceptor substituents). In principle any donor is able to form a compound with any acceptor. It is all determined by the energetics of these processes. The same atom or molecule can act sometimes as a donor, sometimes as an acceptor, depending on its partner.

Donor–acceptor complexes can be classified as follows:

nv ($R_2O \cdot BX_3$)	σv ($RX \cdot BX_3$)	πv ($Ar \cdot BX_3$)
$n\pi$ ($R_2O \cdot Ar$)	$\sigma\sigma$ ($RX \cdot I_2$)	$\pi\sigma$ ($Ar \cdot I_2$)
$n\sigma$ ($R_2O \cdot I_2$)	$\sigma\pi$ ($RX \cdot Ar$)	$\pi\pi$ ($Ar \cdot Ar$).

The largest number of investigations have been concerned with complexes of types $\pi\pi$ and $\pi\sigma$. Comprehensive monographs[4,5] and reviews[6-8] have been published. Complexes with σ-donors have been least studied. As already stated, the present Review will survey mainly the results of our investigations on complexes of types nv, $n\sigma$, and partly πv.

From general ideas on donor–acceptor interaction it may be supposed that the most important parameter, on which the properties of intermolecular bonds and of the complexes largely depend, is the magnitude of the charge transferred from donor to acceptor.

One way to test experimentally the concept of intermolecular bonds as charge-transfer bonds is to investigate the type of relation between the degree of charge transfer and the stability of the resulting bonds. The degree of charge transfer can be assessed from the dipole moment of the intermolecular bond, and the stability from the heat of formation of the complexes. These two parameters will be examined later as the most important for characterising a donor–acceptor bond. The dipole moments of complexes have been investigated quite widely[9], but considerably fewer data are available on their heats of formation[10,11].

2. DETERMINATION OF DIPOLE MOMENTS AND HEATS OF FORMATION OF MOLECULAR COMPOUNDS

The usual method for determining the dipole moments of molecules in dilute solution is not very suitable for the investigation of molecular compounds, owing to possible dissociation into their components[12-15]. In several investigations attempts were made to overcome this difficulty by allowing for the dissociation constant of the complex, which was found by some other method; this necessitated additional experiments, and did not always yield the desired results.

More accurate results can be obtained by a method[16-19] in which the molecular polarisation of the complexes is determined by measuring the dielectric constant and the density (or refractive index) of a series of isomolar solutions. The experimental values of the polarisation for a range in which one component is present in excess, i.e. a range in which dissociation of the complex is suppressed, are extrapolated to infinite dilution. However, this method is extremely laborious, and exhibits the general defects associated with the extrapolation of experimental values of molecular polarisation to infinite dilution.

Dielectrometric titration must be acknowledged as experimentally the simplest method, giving the most accurate results for the dipole moments of molecular compounds[20-22]. It consists essentially in measuring the dielectric constant ϵ and the density d of solutions of the component A in an inert solvent ($C_A \simeq 0.05$–0.1 M) with successive addition of small portions of the component D.

The experiment is conducted in a measuring cell with stirring of the solution, which enables ϵ–C_D and d–C_D curves to be obtained (the latter by a float method) over a wide range of concentrations C_D for the same initial solution of component A. The design of the measuring cell enables experiments to be conducted in an atmosphere of a dry inert gas.

If the components A and D do not interact, linear ϵ–C_D and d–C_D relations are observed. In such case all that is required is to determine the dipole moment of the added substance D in a solvent containing a small quantity of substance A.

If a complex having a different dipole moment from that of the added component D is formed in the system, the dielectrometric titration curve for 1 : 1 complexes of moderate stability usually has the form mnl (Fig. 1). Extrapolation (by Hedestrand's method) of the initial portions of the ϵ–C_D and d–C_D curves gives the dipole moment of the compound AD when dissociation is suppressed. Extrapolation of the second portions of the curves (following the inflection) gives the dipole moment of the added substance D.

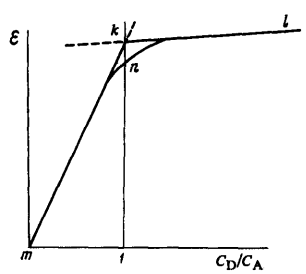


Figure 1. General form of dielectrometric titration curves for systems of the type A + D ⇌ A.D.

The parameters α and β in Hedestrand's equation are determined from the relations

$$\alpha = \frac{\varepsilon_s - \varepsilon_b}{C_{AD}}, \quad \beta = \frac{d_s - d_b}{C_{AD}},$$

where ϵ_s and d_s are the extrapolated values of the dielectric constant and the density of the solution at the point k (Fig.1), and ϵ_b and d_b are the dielectric constant and the density of benzene.

The departure of the experimental curve mnl from the extrapolated mkl is due to dissociation of the complex into its components. The magnitude of this deviation enables the equilibrium constant of the complexing reactions to be determined, and the thermodynamic parameters of the complex from the temperature dependence of the equilibrium constant[23,24].

In the case of complexes which are only slightly dissociated in solution the $\epsilon - C_D$ curves have the form *mkl* (Fig. 1), and dielectrometric titration gives values for the dipole moment which are close to those obtained by the usual method. With complexes which are dissociated the two methods show very substantial differences, the usual method giving incorrect results for the dipole moments in such systems.

Dielectrometric titration will give valuable information on complex formation in more complicated systems than 1 : 1 complexes. For example, investigation of the complexes formed by tin and titanium tetrachlorides with ethers and sulphides revealed that the processes took place in stages. Fig. 2 shows $\epsilon - C_D$ curves for the complexes of tin(IV) chloride with certain sulphides[25]. It is clearly evident that a 1 : 1 complex having a large dipole moment is formed initially when a sulphide is added to a solution of the tin chloride in benzene; this is followed by addition of a second molecule of the sulphide, accompanied by a decrease in the overall dipole moment of the complex. The process is complete with formation of a 1 : 2 complex, and the slope of the straight line following this ratio of the components corresponds to the dipole moment of the added sulphide.

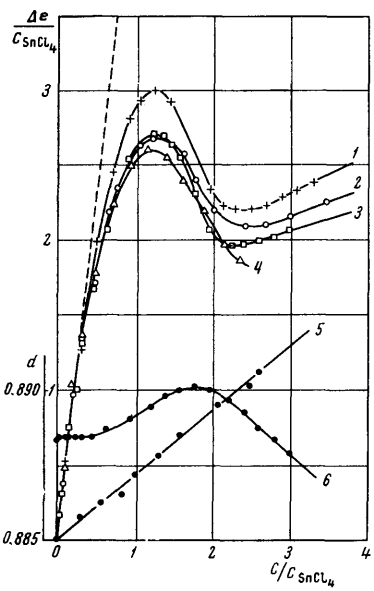


Figure 2. Curves for the dielectrometric titration of 0.05–0.15 M $SnCl_4$ in benzene with:
1) dibutyl sulphide; *2*) dinonyl sulphide; *3*) dioctyl sulphide; *4*) dihexadecyl sulphide; *5*) diphenyl sulphide; *6*) density of solutions of $SnCl_4 + (C_8H_{17})_2S$.

Valuable information on complexing processes has been obtained where more than one donor atom is present. Forward and back titration, e.g. in the aluminium bromide–dioxan system, has enabled the composition, structure, and mutual convertibility of 1 : 1 and 2 : 1 complexes to be established[26]. This procedure may be extremely useful for investigating complex formation by polymer molecules.

Thus dielectrometric titration enables the process of complex formation to be followed, the composition of the resulting complexes to be determined, and their dipole moments to be measured under conditions such that dissociation is suppressed. It is possible by this method to determine the equilibrium constants of the complexing reactions, and from their temperature dependence to find the thermodynamic parameters of the complexes[23,24].

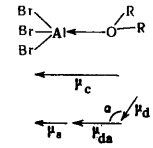
Investigation of the aluminium bromide–benzene system by dielectrometric titration[27] has led to the conclusion that the large dipole moment (exceeding 5 D), usually attributed to a complex of aluminium bromide with benzene, is due to water present as impurity in the benzene and the formation of a highly polar ternary complex $Al_2Br_6.HBr.nC_6H_6$. The true dipole moment of the complex of aluminium bromide with benzene proved to be ~ 1.0 D.

The heat of complex formation in the gas phase, with the energy of rearrangement of donor and acceptor molecules accompanying complex formation taken into account, is a direct measure[10] of the energy of the donor–acceptor bond. Among several methods[5,10] for determining heats of complex formation the most convenient—both experimentally and in the wide range of varied systems covered—is their measurement in solution. However, the effect of the solvent must then be allowed for. Several workers have shown[28–30] that heats of complex formation in inert solvents are close to the values in the gas phase.

Calorimetric titration is the most convenient method for obtaining actual data on heats of formation of molecular compounds which dissociate in solution[31]. Valuable information on the state of the compounds in solution is provided by cryoscopic titration[32]. Correlation of the results obtained by dielectrometry and calorimetry with the results of this method enables more unambiguous answers to be given to the questions of what complex and what state the measured parameters relate to.

3. STRUCTURE OF COMPLEXES OF DONOR–ACCEPTOR TYPE

The overall dipole moment of a complex μ_c can be written as the sum of three terms: $\mu_c = \mu_d + \mu_a + \mu_{da}$, where the right-hand side represents the dipole moments of the donor portion of the complex, the acceptor portion of the complex, and the donor–acceptor bond respectively. With the complex of aluminium bromide and ether, for example, resolution of the overall dipole moments μ_c into its components can be represented by the scheme



Hence, in order to evaluate μ_{da} from the experimental value of μ_c, it is necessary to know the magnitude and the relative orientation of μ_d and μ_a. Since complex formation involves in several cases rearrangement of both acceptor and donor molecules, the experimental data can be analysed provided that the structure of the molecular compounds is known. Structural investigations of complexes also provide information on the type of molecular orbitals involved in the formation of intermolecular bonds.

Extensive X-ray investigations[33,37] of complexes formed by halogens X_2 (Cl_2, Br_2, I_2, ICl) with aromatic hydrocarbons and with compounds containing oxygen, nitrogen, and

sulphur have shown that roughly the same kind of changes in the molecules accompany complex formation in all these systems.

In all X_2.D complexes the donor–acceptor bond X← D is located in line with the X–X bond: X–X←D has an XXD angle of 178–180°. Thus the two halogen atoms in the complex are not equivalent. The length of the X–X bond increases on complex formation, the elongation being greater the more stable the complex. Thus in the comparatively stable complexes formed by iodine with dibenzyl sulphide and with trimethylamine the increase in length of the iodine–iodine bond is 0.15 and 0.20 Å respectively. In the less stable complexes formed by chlorine and by bromine with benzene the X–X bonds are of practically the same length as in the free molecules. The lengths of the intermolecular bonds X–D are also associated with the stability of the complexes.

The orientation of donor molecules relative to the donor–acceptor bond differs with amines, ethers and sulphides.

The complex of dibenzyl sulphide with iodine[34] has an angular configuration (Fig. 3). The mirror plane of the molecule passes through the I–I←S line between the benzyl groups. The interatomic distances and angles in the sulphide molecule remain practically unchanged on complex formation. An analogous angular configuration has been found[35,36] in the complex of iodine with dithian. The angular configuration of the complexes formed by iodine with sulphides can be regarded as evidence that the donor pair of electrons in the sulphide molecule is the $3p^2$ lone pair of the sulphur atom.

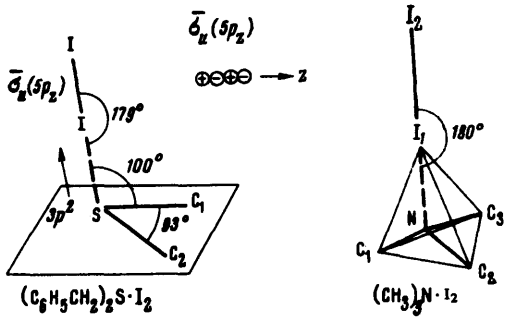


Figure 3. Structure of the complexes $(C_6H_5CH_2)_2S.I_2$ and $(CH_3)_3N.I_2$.

The trimethylamine molecule has a tetrahedral configuration[37] ($\alpha = 180°$) in its complex with iodine (Fig. 3). This indicates that the lone pair of electrons of the nitrogen atom takes part in the intermolecular bond in the sp^3 state.

The valency angle of oxygen in its complexes with halogens is not reliably known. X-Ray examination of the complex of dioxan with iodine chloride yields[38] 178° for the OICl angle, and a value of 160° has been found[39] from examination of the complex of dioxan with iodine.

X-Ray and electron-diffraction investigations of the complexes formed by boron trifluoride with amines[40–42] and with diethyl ether and by aluminium bromide with hydrogen sulphide[43] have shown that the acceptor portion of these complexes has a tetrahedral conformation. The amine molecules undergo no fundamental rearrangement on complex formation with boron trifluoride. Thus the angles at the nitrogen in the complexes formed by this halide with ammonia, methylamine, and trimethylamine are close to the tetrahedral angles (107–114°), while the length of the carbon–nitrogen bond in trimethylamine is 1.50 Å,[41] these being close to the parameters in free trimethylamine. The lengths of the boron–nitrogen, boron–oxygen, and aluminium–sulphur donor–acceptor bonds (1.53–1.60,[41,42] 1.52,[40] and 2.40 [43] Å) are close to or slightly exceed the sum of the covalent radii (1.58, 1.54, and 2.30 Å respectively).

Little work has been done on establishing the structure of the complexes formed by tetrahalides of Group IV metals. Tin and titanium tetrahalides give with oxygen and sulphur compounds complexes of two types—MX_4.D with five-coordination of the metal atom, and MX_4.2D with six-coordination of the metal—the process of complex formation taking place in stages[22,35,44,45].

It has been established by means of dipole moments that $TiCl_4.R_2S$ complexes[46] have the tetragonal pyramidal conformation *I* (Fig. 4), and $SnCl_4.R_2S$ complexes the trigonal bipyramidal conformation *II*. A bipyramidal structure has been found also by X-ray analysis for the 1 : 1 complex of trimethyltin chloride with pyridine[47].

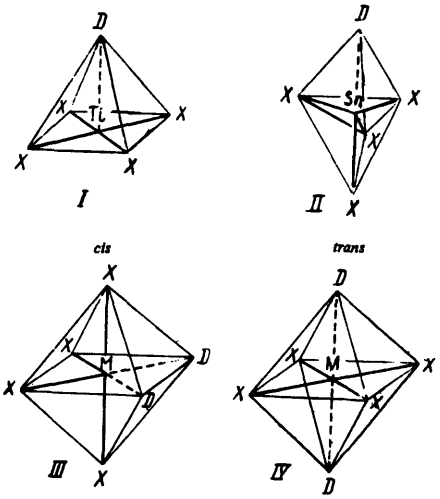


Figure 4. Conformation of complexes of tin and titanium tetrahalides.

For compounds having the composition MX_4.2D an octahedral conformation is the most probable, two isomers being possible here, with the donor molecules in *cis*- and *trans*-positions in the octahedron (*III* and *IV*, Fig. 4). An octahedral structure with *cis*-arrangement of the donor molecules has been established by X-ray examination for the complex $SnCl_4.2POCl_3$.[48] The same structure has been found for the complexes $SnCl_4.2SeOCl_2$ [49] and $TiCl_4.2POCl_3$.[50] A *cis*-octahedral structure has been established also for the dimeric compounds $SnCl_3OCH_3.CH_3OH$ and $SnBr_3OCH_3.CH_3OH$.[51] In contrast to this, a *trans*-octahedral conformation has been found[52] for the complex of tin tetrachloride with tetrahydrothiophen $SnCl_4.2C_4H_8S$.

The first use has been reported[53] of nuclear quadrupole resonance (n.q.r. of halogen atoms) for solving problems of *cis–trans*-isomerism in octahedral complexes. It has been established by the method of molecular orbitals that the n.q.r. frequency shifts and the character of the n.q.r. splittings differ for *cis*- and *trans*-isomers of octahedral complexes of Group IV metal halides with *n*-donors. Fig.5 illustrates the relation between the structure of the isomers and the corresponding form of n.q.r. spectra. Fig. 5 includes also a suggested scheme of splitting for the bipyramidal complex $MX_4.D$, in which the coordination number of the metal is 5. The large splitting in the spectrum of the *cis*-isomer has been found to be due to the chemical non-equivalence of axial and equatorial halogen atoms.

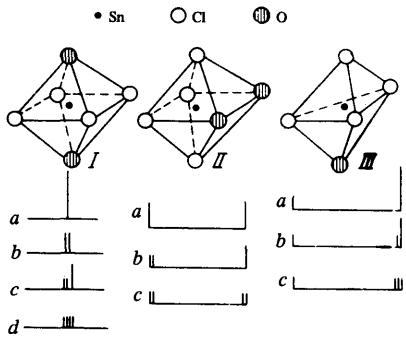


Figure 5. Splitting of nuclear quadrupole resonance spectra of complexes formed by tetrahalides of Group IV metals with *n*-donors.

The structure of several complexes of tin(IV) chloride has been established from the character of the splitting in the n.q.r. spectra: n.q.r. data[53] show that the complexes $SnCl_4.2POCl_3$ and $SnCl_4.2C_2H_5OH$ have the *cis*-structure *III* (Fig. 4), the complex $SnCl_4.2(C_2H_5)_2O$ has the *trans*-structure *IV* (Fig. 4), and the complexes $SnCl_4.CH_3O[CH_2]_2OCH_3$ and $SnCl_4.CH_3O[CH_2]_4OCH_3$ have a *trans*-chain structure (Fig. 6).

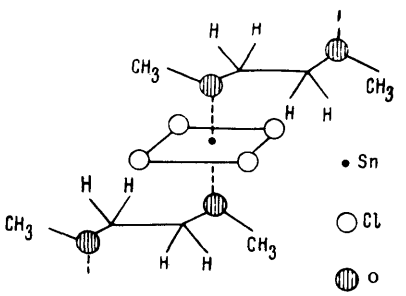


Figure 6. Structure of the complex $SnCl_4.CH_3O[CH_2]_2OCH_3$ in the solid state.

It may be noted that data on the structure of complexes obtained by X-ray examination and from nuclear quadrupole resonance, as well as most of the published data obtained by infrared spectroscopy[54–58], relate to the crystalline solid state. The method of dipole moments enables an assessment to be made of the state of complexes in solution.

A detailed investigation of the complexes formed by titanium tetrachloride with various sulphides led to the conclusion[45] that, in solution, the octahedral complexes $TiCl_4.2R_2S$ consist of a mixture of *cis*- and *trans*-isomers (*III* and *IV*, Fig. 4), with an approximately random distribution of donor molecules among the apices of the octahedron.

The dipole moments suggest that the complexes $SnCl_4.2R_2S$ are also present in solution (in benzene) as a mixture of *cis*- and *trans*-isomers[46]. On crystallisation the equilibrium may be displaced towards formation of either form. Such a situation is observed, for example, in the tin(IV) chloride–thiolan system: in benzene the complex $SnCl_4.2C_4H_8S$ is a mixture of isomers (dipole moment 5.0 [44]), but in the solid state it has the *trans*-structure[52].

Extremely interesting results have been obtained from an investigation of the complexes $SnCl_4.RO[CH_2]_2OR$ in benzene (dipole moments) and in the solid state (n.q.r.). Compounds of the type $RO[CH_2]_nOR$ or $RS[CH_2]_nSR$, whose molecules contain two donor atoms, enable octahedral complexes of definitely *cis*-structure to be obtained with titanium and tin tetrachlorides at values of $n = 2, 3$. The dipole moments of such complexes reach 9–10 D.[45,46,59] It was found that in benzene the complex $SnCl_4.RO[CH_2]_2OR$ was monomeric and had the *cis*-structure, and in the crystalline state it had a *trans*-chain structure[53].

Thus all the results obtained indicate unambiguously that the structure of octahedral complexes formed by tetrahalides of Group IV metals with *n*-donors may change on passing from one state to another. The character of the changes differs in different systems. This fact was further taken into account when considering the experimental dipole moments of the complexes.

4. DEGREE OF CHARGE TRANSFER AND STABILITY OF INTERMOLECULAR BONDS

Examination of the dipole moments and heats of formation of complexes formed by iodine with organic sulphides varying in structure has led[24,60] to the establishment of direct proportionality between the dipole moments of intermolecular bonds (μ_{da}) and the heats of formation of the complexes ($-\Delta H$). A similar $\mu_{da}-\Delta H$ relationship has been found in complexes formed by tin tetrachloride with organic sulphides[46]. It has been confirmed[61] for the complexes formed by iodine with amines and with ethers.

The value of μ_{da} is in general a complicated function of several parameters. Besides the displacement of electron density from donor to acceptor, a dipole moment may appear here, as in ordinary chemical bonds, as a result of a difference in size of the atoms, of a state of hybridisation. Contributions due to the difference in size of the atoms forming the bond (homopolar dipole) and to the change in hybridisation of the *n*-donors (atomic dipole) are probably small, especially as the molecules of donors (amines, ethers, sulphides) do not undergo any substantial changes on complex formation. Hence it may be assumed to a first approximation that the main contribution to the value of μ_{da} is made by the displacement of electron density from donor to acceptor, or the degree of charge transfer. The latter can be determined from the experimental values of μ_{da} and the interatomic distances r as the ratio μ_{da}/er, where e is the charge on the electron.

An attempt has been made[62] to ascertain whether a linear relation between μ_{da}/er and ΔH is characteristic of

narrow series of analogous complexes or whether it is general for the complexes under discussion. The range of materials investigated was therefore considerably extended, by determining the dipole moments and heats of formation of the complexes formed by tin and titanium tetrachlorides and tetrabromides with sulphides, ethers, and nitriles. Published data on the dipole moments and the heats of formation of the complexes were surveyed.

Table 1. Dipole moments, degrees of charge transfer, and heats of formation of donor–acceptor bonds in complexes[62].

No.	Complex	μ_c	μ_d	μ_{da}	r	$\frac{\mu_{da}}{er}$	ΔH
1	$I_2 \cdot (C_2H_5)_2O$	1.9	1.21	1.4	2.60	0.11	4.3
2	$I_2 \cdot C_5H_{10}O$	2.82	1.63	1.8	2.60	0.14	4.9
3	$I_2 \cdot C_4H_8O$	3.00	1.70	2.0	2.60	0.16	5.3
4	$I_2 \cdot (C_2H_5)_2S$	1.99	1.56	0.4	2.78	0.03	0.3
5	$I_2 \cdot (C_2H_5)_2S$	3.64	1.44	2.0	2.78	0.15	4.6
6	$I_2 \cdot (C_2H_5CH_2)_2S$	3.78	1.38	2.2	2.78	0.16	4.8
7	$I_2 \cdot (i\text{-}C_5H_{17})_2S$	4.72	1.63	3.1	2.78	0.23	7.4
8	$I_2 \cdot (i\text{-}C_7H_{15})_2S$	4.90	1.63	3.4	2.78	0.25	8.1
9	$I_2 \cdot (C_2H_5)_2S$	4.62	1.60	3.1	2.78	0.23	7.8
10	$I_2 \cdot (C_2H_7)_2S$	4.90	1.55	3.4	2.78	0.25	8.1
11	$I_2 \cdot (C_4H_9)_2S$	5.0	1.57	3.6	2.78	0.27	7.6
12	$I_2 \cdot (C_6H_{11})_2S$	5.34	1.58	3.8	2.78	0.28	7.0
13	$I_2 \cdot (C_{16}H_{17})_2S$	5.07	1.58	3.5	2.78	0.26	7.4
14	$I_2 \cdot C_4H_8S$	5.49	1.87	3.9	2.78	0.29	10.0
15	$I_2 \cdot (C_4H_{11})_2S$	5.44		4.0	2.78	0.30	10.5
16	$I_2 \cdot (C_2H_5CH_2)_3N$	2.80	0.65	1.1	2.30	0.10	2.3
17	$I_2 \cdot C_5H_5N$	5.70	2.02	2.7	2.30	0.24	7.5
18	$I_2 \cdot C_9H_7N$	5.70	2.25	2.5	2.30	0.23	7.1
19	$I_2 \cdot C_6H_5NH_2$	6.07	1.4	3.4	2.30	0.31	8.4
20	$SnCl_4 \cdot C_2H_5O(CH_2)_4OC_2H_5$	6.63	1.65	1.7	2.27	0.16	6.7
21	$SnCl_4 \cdot CH_3O(CH_2)_3O(CH_2)_3OCH_3$	8.15	1.91	2.8	2.27	0.26	10.7
22	$SnCl_4 \cdot C_2H_5O(CH_2)_3OC_2H_5$	9.24	1.63	3.5	2.27	0.32	10.9
23	$SnCl_4 \cdot C_2H_5O(CH_2)_3OC_2H_5$	8.82	1.65	3.2	2.27	0.29	11.9
24	$SnCl_4 \cdot C_4H_9O(CH_2)_3OC_4H_9$	9.18	1.60	3.5	2.30	0.32	11.5
25	$SnCl_4 \cdot C_4H_9SC_2H_5$	4.20	1.48	0.9	2.56	0.07	2.0
26	$SnCl_4 \cdot (C_6H_5CH_2)_2S$	4.77	1.38	1.5	2.56	0.12	3.8
27	$SnCl_4 \cdot (C_3H_7)_2S$	6.49	1.55	3.3	2.56	0.27	12.9
28	$SnCl_4 \cdot (C_4H_9)_2S$	6.71	1.57	3.5	2.56	0.28	12.6
29	$SnCl_4(C_6H_{17})_2S$	6.79	1.58	3.6	2.56	0.29	11.9
30	$SnCl_4(i\text{-}C_8H_{17})_2S$	3.76	1.63	0.4	2.56	0.03	0.4
31	$SnCl_4 \cdot C_4H_9SCH_2SC_4H_9$	8.42	1.34	2.7	2.56	0.22	7.3
32	$SnCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	9.96	2.02	3.9	2.56	0.32	12.6
33	$SnCl_4 \cdot C_4H_9S(CH_2)_3SC_4H_9$	10.82	1.89	4.4	2.56	0.36	13.7
34	$SnCl_4 \cdot CH_3CN$	7.63	3.40	1.2	2.20	0.11	7.0
35	$SnCl_4 \cdot C_6H_5CN$	8.40	3.90	1.5	2.20	0.14	6.1
36	$TiCl_4 \cdot C_6H_5CN$	7.08	3.90	3.1	2.13	0.30	11.5
37	$TiCl_4 \cdot (C_6H_5)_2O$	3.67	1.22	2.5	2.18	0.24	6.0
38	$TiCl_4 \cdot (C_6H_{17})_2O$	3.83	1.22	2.6	2.18	0.25	6.3
39	$TiCl_4 \cdot C_5H_{10}O$	4.52	1.87	3.1	2.18	0.30	12.0
40	$TiCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	7.77	1.65	3.3	2.18	0.31	11.9
41	$TiCl_4 \cdot C_4H_9O(CH_2)_2OC_4H_9$	8.23	1.60	3.6	2.18	0.34	12.9
42	$TiCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	8.16	1.63	3.6	2.18	0.34	11.6
43	$TiCl_4 \cdot C_4H_9S$	4.54	1.71	4.1	2.47	0.34	12.0
44	$TiCl_4 \cdot (C_4H_9)_2S$	4.66	1.58	4.3	2.47	0.36	11.5
45	$TiCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.78	1.89	4.1	2.47	0.34	12.6
46	$TiCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.31	2.02	3.7	2.47	0.31	11.0
47	$SnBr_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	10.25	1.89	4.2	2.56	0.34	10.0
48	$TiBr_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.42	2.02	3.9	2.47	0.33	10.3
49	$TiBr_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	7.70	1.65	3.4	2.18	0.32	10.6
50	$BF_3 \cdot (CH_3)_2O$	4.35	1.25	2.8	1.54	0.38	13.7
51	$BF_3 \cdot C_4H_8O$	5.68	1.70	3.4	1.54	0.46	16.8
52	$B(CH_3)_3 \cdot NH_3$	4.15	1.30	2.6	1.58	0.34	13.8
53	$B(CH_3)_3 \cdot N(CH_3)_3$	3.92	0.75	2.9	1.58	0.38	17.6

Since the relationship proved to be general in character, it appears desirable to examine the results of this work in greater detail. Table 1 gives the formulae of the complexes, the values of μ_c, μ_d, μ_{da}, and r, and also the parameters μ_{da}/er and the heats of formation ΔH per donor–acceptor bond. In the determination of μ_{da} (see scheme at beginning of Section 3) from the experimental values of μ_c, account was taken of the structure of the complex and the values of μ_d and μ_a. The molecules of amines, ethers, sulphides, and nitriles give donor–acceptor bonds involving the lone pair of the corresponding heteroatom. It can be assumed to a first approximation that μ_d in the complex is equal to the dipole moment of the initial molecule. With regard to the relative arrangement of the μ_d and μ_{da} vectors, it follows from what has been said above that the angle α between them can be taken to be 100° in the sulphide complexes, 150–160° in the ether complexes, and 180° in the complexes with amines and nitriles.

The dipole moments of the acceptor part of the complexes μ_a were determined in conformity with the structure of the complex and the moments of the M–Hal bonds. The conformation of a tetragonal pyramid (*I*, Fig. 4) was adopted for the five-coordinate complexes $TiX_4.D$, a trigonal bipyramid (*II*) for the five-coordinate complexes $SnCl_4.D$, and an octahedral conformation for the six-coordinate complexes $MX_4.2D$. For the third group, only data relating to complexes of definitely *cis*-structure (*III*, Fig. 4) have been considered. The dipole moments of the M–X bonds were taken to be as follows[65]: Sn–Cl 3.0 D, Sn–Br 2.9 D, Ti–Cl 2.2 D, and Ti–Br 2.1 D.

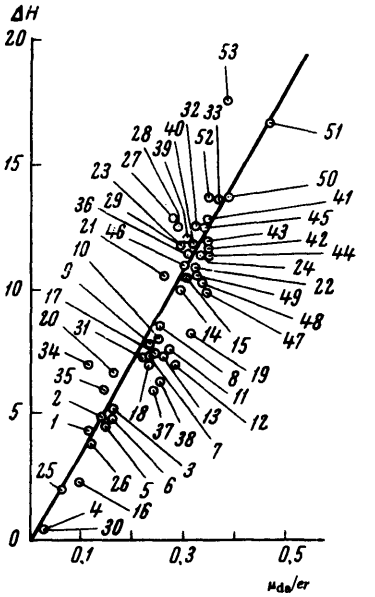


Figure 7. Dependence of ΔH on μ_{da}/er for complexes of I_2, $SnCl_4$, $SnBr_4$, $TiCl_4$, $TiBr_4$, $(CH_3)_3B$, and BF_3 with amines, ethers, and sulphides (numbering of points corresponds to Table 1.).

A tetrahedral structure was adopted[40] for the complexes formed by boron trifluoride with dimethyl ether and with tetrahydrofuran and by trimethylboron with ammonia and with trimethylamine, the bond dipole moments being 1.6 D for the boron–fluorine bond[64,65] and 0.3 D for the boron–methyl bond[65].

The data in Table 1 show that a definite relation exists between the parameters μ_{da}/er and the heats of formation of the coordinate bonds $-\Delta H$: the greater the degree of charge transfer, the larger the heat of formation, and hence the more stable the intermolecular bond. This is especially clearly evident from Fig. 7.

The equation to the straight line, found by the method of least squares, is

$$\Delta H = 35.3 \frac{\mu_{da}}{er} \qquad (1)$$

The results in Table 1 cover more than fifty diverse systems. From this it may be concluded that the relation established between the degree of charge transfer and the stability of the intermolecular bond is general for donor–acceptor complexes of type $n\nu$, $n\sigma$.

The direct proportionality between the degree of charge transfer and the energy of formation of a coordinate bond can be regarded as quantitative evidence of the correctness of the view that intermolecular bonds of this type are charge-transfer bonds.

A theoretical basis for the experimental relation (1) can be obtained from Mulliken's theory of charge-transfer complexes[1,3]. The wave function of the ground state of a complex A.D is written to a first approximation in the form

$$\psi = a\psi_0(\mathrm{A, D}) + b\psi_1(\mathrm{A^- — D^+}) \qquad (2)$$

in which ψ_0 is the wave function of the "bondless" structure and ψ_1 the wave function corresponding to the structure with transfer of charge. Solution of this equation for the case in which $a > b$ gave relations[1] between certain parameters of the complexes.

On the basis of these relations the equation

$$\Delta H = \frac{h\nu}{a^2\left(1+\frac{a}{b}S_{01}\right)\left(1+\frac{b^2}{a^2}+\frac{b^{*2}}{a^{*2}}\right)} \cdot \frac{\mu_{da}}{er} \qquad (3)$$

has been deduced[24,61], linking the degree of charge transfer μ_{da}/er with the energy of formation of the complex ΔH. Here $h\nu$ is the energy of the electronic transition corresponding to the charge-transfer band, a and b are the coefficients in Eqn. (2), a^* and b^* are the coefficients in the analogous equation describing the excited state, and $S_{01} = S\psi_1\psi_0 d\tau$ is the overlap integral of the functions ψ_0 and ψ_1 (Eqn. 2).

The large majority of investigations[4–6] on charge-transfer complexes have involved studying the corresponding ultraviolet or visible absorption bands. Equation (3) shows how the position of the charge-transfer band is related to the degree of charge transfer and the energy of the intermolecular bond. It enables experimental values of μ_{da}/er and ΔH to be used to predict the position of the corresponding bands. This is of great value, especially in view of the fact that hardly any work has been done on charge-transfer bands for complexes of type $n\nu$.

The necessary and sufficient condition for a linear relation between μ_{da}/er and ΔH is that the coefficient

$$\frac{h\nu}{a^2\left(1+\frac{a}{b}S_{01}\right)\left(1+\frac{b^2}{a^2}+\frac{b^{*2}}{a^{*2}}\right)} = K \qquad (4)$$

should be constant for different complexes. The problem of the constancy of K (Eqns. 3 and 4) for different complexes, and how close it is to the slope (35.5 kcal or 1.5 eV) of the experimental straight line (1), can be approached in various ways.

We can use the charge-transfer bands $h\nu$ known for certain complexes to calculate K (Eqn. (4) and compare the result with the experimental value (1). Or, if the charge-transfer bands are unknown, we can start with experimental values of ΔH and μ_{da}/er, predict the position of the bands by means of Eqn. (3), and verify the result experimentally.

Corresponding calculations of K using values of $h\nu$ for a series of iodine complexes have shown[62] entirely satisfactory agreement with the experimental value of K. In addition, experimental values of μ_{da}/er and ΔH have been used to predict and to find previously unknown charge-transfer bands in a series of complexes of tin and titanium tetrachlorides with ethers and sulphides.

It has been shown that the experimentally established linear relation between degree of charge transfer and energy of the donor–acceptor bond can be described by Eqn. (3), obtained on the basis of Mulliken's theory.

The presence of direct proportionality between values of ΔH and μ_{da} for the same acceptor with a group of similar donors can be used to estimate values of μ_a. In this way dipole moments have been determined[62] for the iodine molecule in complexes with sulphides and amines (0.8–1.0 D). These values have been taken into account in determining μ_{da} in the corresponding complexes. An analogous estimate[62] of the dipole moment of the tin–chlorine bond in five-coordinate complexes of tin(IV) chloride with organic sulphides gives 3.0 D, practically identical with the dipole moment of this bond in the tin tetrachloride molecule[63].

5. DONOR PROPERTIES OF AMINES, ETHERS, AND SULPHIDES

Two aspects of the problem of the donor properties of molecules containing a heteroatom—the influence of the structure of the molecule on the donor properties of the heteroatom and the comparative donor properties of amines, ethers, and sulphides of similar structure—will be considered. The effect of molecular structure on donor properties is revealed most clearly in sterically unhindered complexes. The complexes formed by iodine with amines, ethers, and sulphides meet these requirements most closely.

Table 2. Dipole moments and dissociation constants of complexes of iodine with sulphides.

Complex	μ	$10^{-3}K$	Complex	μ	$10^{-3}K$
$(C_2H_5)_2S\cdot I_2$	4.62	4.0	$(C_3H_5)_2S\cdot I_2$	3.64	2.0
$(C_3H_7)_2S\cdot I_2$	4.90	3.4	$C_4H_8S\cdot I_2$	5.49	1.2
$(C_4H_9)_2S\cdot I_2$	5.00	2.7	$2.5(CH_3)_2C_4H_8S\cdot I_2$	5.76	1.4
$(C_5H_{11})_2S\cdot I_2$	5.37	3.1	$(C_6H_5CH_2)_2S\cdot I_2$	3.78	2.3
$(C_8H_{17})_2S\cdot I_2$	5.07	1.6	$(C_6H_{11})_2S\cdot I_2$	5.44	2.3
$(C_9H_{19})_2S\cdot I_2$	5.23	1.9	$C_4H_4S+I_2$	0.42*	—
$(C_{10}H_{21})_2S\cdot I_2$	4.78	0.8	$(C_6H_5)_2S+I_2$	1.99*	—
$(C_{16}H_{33})_2S\cdot I_2$	4.35	0.3	$C_6H_5SCH_3+I_2$	1.88*	—
$(i\text{-}C_4H_9)_2S\cdot I_2$	5.15	4.7	$C_6H_5SC_2H_5+I_2$	2.63*	—
$(i\text{-}C_5H_{11})_2S\cdot I_2$	5.06	1.9	$C_6H_5SC_{10}H_7+I_2$	1.75*	—
$(i\text{-}C_5H_{11})SC_4H_9\cdot I_2$	5.12	1.4	$(C_2H_5)_2S_2+I_2$	2.48*	—
$(s\text{-}C_7H_{15})_2S.I_2$	4.90	1.4	$(C_2H_5)_2S_3+I_2$	2.24*	—
$(s\text{-}C_8H_{17})_2S.I_2$	4.72	1.0	$C_2H_5S(CH_2)_2SC_2H_5\cdot 2I_2$	5.50	—

* Dipole moments of the sulphides in the presence of iodine (~0.04 M).

Table 2 gives[66] dipole moments and dissociation constants for complexes of iodine with sulphides of different structures. Various dialkyl sulphides (C_2–C_{16}) both straight-chain and iso-structures, form with iodine complexes of almost identical stability, their dipole moments being 4.6–5.6 D.

In contrast, aromatic and $\alpha\beta$-unsaturated sulphides exhibit very weak donor properties towards iodine. The dipole moments of diphenyl sulphide and thiophen, measured in the presence of iodine (0.05–0.1 M), are close to the values in the pure solvent. Proof that the diminution in donor properties in this case is not due to steric hindrance is provided by the fact that the saturated analogues—dicyclohexyl sulphide and thiolan—form with iodine under

the same conditions stable compounds having dipole moments and dissociation constants close to the corresponding values for complexes of iodine with dialkyl sulphides.

If the C=C double bond or the aromatic ring is moved away from the sulphur atom, as occurs in $\beta\gamma$-unsaturated compounds, the sulphur atom is able to form a donor–acceptor bond with iodine. Dibenzyl sulphide and diallyl sulphide behave towards iodine in a fundamentally similar manner to dialkyl sulphides, but the dipole moments of the complexes are considerably smaller.

The differences in the behaviour of $\alpha\beta$- and $\beta\gamma$-unsaturated compounds of sulphur compared with saturated compounds is probably explained by a greater or smaller degree of interaction of the lone pair of electrons of the sulphur atom, responsible for complex formation, with the π-electrons of the unsaturated systems.

Table 3. Dipole moments and thermodynamic constants of complexes I_2.D of iodine with amines, sulphides, and ethers.

Donor	μ_c	μ_{da}	$-\Delta H$	$-\Delta S$	$-\Delta F_{298°}$	$K_{298°}$
Triethylamine	10.50	9.7	—			
Tripentylamine	8.50	7.2	12.3			
Trioctylamine	8.20	6.0	12.2			
Butylamine	6.07	4.4	8.4			
Pyridine	5.70	3.7	6.0	9.4	3.2	222
Quinoline	5.70	3.5	5.6	7.4	3.4	300
Tribenzylamine	2.80	2.1	2.3			
Triphenylamine	—	—	1.1			
Thiophan **	5.49	4.7	10.0			
Dicyclohexyl sulphide	5.44	4.8	10.5	23.1	3.6	435
Diethyl sulphide	4.62	3.9	7.8	15.9	3.4	310
Dipropyl sulphide	4.90	4.2	8.1	15.8	3.4	294
Dibutyl sulphide	5.00	4.4	7.6	13.6	3.6	385
Dipentyl sulphide	5.34	4.6	7.0	11.7	3.5	360
Dioctyl sulphide	5.07	4.3	7.4	11.6	3.9	746
Di-s-heptyl sulphide	4.90	4.2	8.1	14.0	3.9	714
Di-s-octyl sulphide	4.72	3.9	7.4	11.0	4.1	1000
Dibenzyl sulphide	3.78	3.0	4.8	3.3	3.8	614
Diallyl sulphide	3.64	2.8	4.6	3.0	3.7	500
Thiophen	0.42*	0	0.4			
Diphenyl sulphide	1.99*	0.4	0.3			
Tetrahydrofuran	3.00	2.0	5.3			
Tetrahydropyran	2.82	1.8	4.9			
Diethyl ether	1.9	1.4	4.3			
Phenetole	—	—	0.5			

* Dipole moments of the sulphides measured in the presence of iodine.

** It is not clear whether thiophen or tetrahydrothiophen is intended here (Ed. of Translation).

Analysis of experimental data on the effect of the structure of the radicals on the donor properties of the heteroatom has shown that the Hammett–Taft rule is satisfied in sterically unhindered complexes. For complexes of iodine with sulphides the equation[25,26] is $-\Delta H = 7.7 - 6.7\,\Sigma\sigma^*$. The large value (6.7) of the coefficient indicates that the complexing reactions are very sensitive to change in the electron density on the heteroatom. An analogous effect of molecular structure on the donor properties of the heteroatom is observed in complexes of iodine with amines and with ethers[24,61,67], as is well illustrated by the data in Table 3.

Complexes with other acceptors, however, begin to exhibit the effect of the steric factor, which makes corrections necessary. The length and the branching of the aliphatic radicals R in ethers ROR have been shown[59] to have an immense influence on their complexing power towards tin(IV) chloride. In the analogous but more stable complexes of the latter with sulphides[22,25,46] the effect of the steric factor is less important, the size of the heteroatom also being of significance.

With aluminium tribromide and also with gallium trichloride aliphatic amines, ethers, and sulphides, independently of the length or degree of branching of the radicals, form complexes having approximately the same degree of charge transfer and stability of their intermolecular bonds[21,68,69].

The donor (or basic) properties of ethers and amines are often assessed from the displacement of the γ_{OD} band in the infrared spectrum of deuteriomethanol on interaction of the latter with the donor (Gordy's method). It is clear from the above that the basicity sequences obtained by this method may be completely different when other acceptors are used. This must be borne in mind in interpreting experimental data in terms of donor–acceptor interaction.

Let us compare the donor properties of amines, ethers, and sulphides of analogous structure. From the ionisation potentials of amines, sulphides, and ethers of similar composition (Table 4) it may be expected that, according to the degree of charge transfer and the stability of the intermolecular bonds with the same acceptor, the sequence of the compounds will be amines > sulphides > ethers. Such a sequence of donor properties is actually observed in the complexes with iodine[61] and tin(IV) chloride[62] and bromide[62].

Table 4. Ionisation potentials (eV) of some amines, sulphides, and ethers[70,71].

Amines	I	Sulphides	I	Ethers	I
$(CH_3)_3N$	7.82	$(CH_3)_2S$	8.68	$(CH_3)_2O$	10.0
$(C_2H_5)_3N$	7 50	$C_2H_5SCH_3$	8.55	$C_2H_5OCH_3$	9.81
$(C_3H_7)_3N$	7.23	$(C_2H_5)_2S$	8.48	$(C_2H_5)_2O$	9.53

In the complexes with titanium(IV) chloride and bromide[62] ethers and sulphides have closely similar donor properties, but in the complexes with aluminium tribromide and trichloride the sequence changes, ethers proving to be stronger donors than are sulphides. According to the degree of charge transfer and the stability of the intermolecular bonds the complexes are arranged in the sequence[68,69]

$$AlBr_3 \cdot R_3N > AlBr_3 \cdot R_2O > AlBr_3 \cdot R_2S\ .$$

The same sequence is observed in the complexes with boron trifluoride[68].

The question arises why ethers, which have a higher ionisation potential than have sulphides, are more active donors towards aluminium and boron halides than are the corresponding sulphides. A possible explanation, that this is due to the specific character of halides of Group III elements, in particular their strength as acceptors, is untenable, since in the complexes with gallium trichloride the strength of the donor–acceptor bonds and the degree of charge transfer vary in the sequence[21,68]

$$GaCl_3 \cdot R_3N > GaCl_3 \cdot R_2S > GaCl_3 \cdot R_2O\ .$$

Sulphides are more active donors than are ethers towards gallium trichloride. A similar sequence[72] of variation in donor properties is found in the gallium tribromide and tri-iodide complexes.

An extremely important factor in the formation of ordinary chemical bonds, by means of a pair of electrons in the

field of two nuclei, is the degree of overlap of the corresponding orbitals. This factor has been found to play a quite important part also in the formation of donor–acceptor bonds. Table 5 gives the overlap integrals of the corresponding orbitals involved in the formation of intermolecular bonds, calculated by the Slater approximation[73].

Table 5. Overlap integrals of intermolecular bonds.

Acceptor	Donor				Experimental sequences	Ref.
	N($2sp^3$)	S($3p$)	O($2sp^3$)	O($2sp^2$)		
I ($5p$)	0.29	0.23	0.14	0.14	I—N>I—S>I—O	24.61
Sn ($5d^2sp^3$)	0.42	0.36	0.28	—	Sn—N>Sn—S>Sn—O	62
Ti ($3d^24sp^3$)	—	0.36	0.38	—	Ti—S≃Ti—O	62
Ga ($4sp^3$)	0.49	0.41	0.41	0.43	Ga—N>Ga—S—Ga—O	68
Al ($3sp^3$)	0.48	0.38	0.42	0.40	Al—N>Al—O>Al—S	68.69
B ($2sp^3$)	0.60	0.47	0.54	0.52	B—N>B—O>B—S	68
O—H($1s$)	0.48	0.36	0.42	0.43	O—H...N>OH···O>OH...S	

In the complexes of amines, sulphides, and ethers with iodine and with tin tetrahalides the overlap integrals vary in the same sequence as do the ionisation potentials of the corresponding donors. These two factors operate in the same direction, ensuring the sequence—amines > sulphides > ethers—for the donor properties. In the complexes of titanium tetrahalides the overlap integrals are closely similar with ethers and with sulphides. This is probably the main reason for the almost identical stability of the intermolecular bonds in complexes of titanium(IV) chloride and bromide with ethers and with sulphides.

Gallium–sulphur and gallium–oxygen intermolecular bonds have equal overlap integrals. Here the sequence of donor properties—amines > sulphides > ethers—corresponds to the differences in the ionisation potentials.

In the complexes of boron and aluminium halides the overlap integrals of the aluminium–oxygen intermolecular bonds are larger than those of the aluminium–sulphur bonds. This fact obviously plays a decisive part and is responsible for the greater stability of the bonds in ether than in sulphide complexes, in spite of the opposite relationship of the ionisation potentials. It is interesting that the same sequence of donor properties—amines > ethers > sulphides—is observed also with hydrogen bonds. Preliminary calculations of the overlap integrals of the corresponding orbitals (Table 5) confirm this sequence.

Comparison of data (Table 5) relating to aluminium and boron halides with those for systems containing hydrogen bonds shows that the observed relationship of the donor properties of ethers and sulphides is not linked with the strength of the acceptor, as would appear at first glance, but is actually determined by the degree of overlap of the corresponding orbitals.

Thus the results which have been cited show that the conditions of overlap of the orbitals involved in the formation of intermolecular bonds are of paramount significance in the formation of donor–acceptor bonds, and in considerable measure determine the properties of the latter.

When the donor properties of various compounds containing a heteroatom are to be compared, account must be taken of the whole set of parameters governing the formation of intermolecular donor–acceptor bonds.

6. DETERMINATION OF ENERGY OF P_π-CONJUGATION IN AROMATIC COMPOUNDS CONTAINING A HETEROATOM BY THE METHOD OF COMPLEX FORMATION

Investigation of the donor power of amines, ethers, and sulphides towards iodine, and of ethers and sulphides towards tin and titanium tetrahalides, has shown that aromatic compounds, unlike aliphatic compounds, do not give with these acceptors complexes which are stable in solution. The chief reason for the marked weakening of the donor properties of aromatic compared with aliphatic compounds is, as mentioned above, interaction of the lone pair of electrons of the heteroatom responsible for complex formation with the system of π-electrons of the aromatic radicals (p_π-conjugation).

In contrast to the above, relatively weak acceptors—the halides of aluminium, gallium, and also boron—yield with aromatic amines, ethers, and sulphides stable complexes, whose dipole moments are close to those of the corresponding complexes with aliphatic donors.

Detailed investigation of the properties of the complexes formed by aluminium tribromide and gallium trichloride with aromatic compounds has shown[68,74–76] that the formation of intermolecular bonds is accompanied by the breakdown of p_π-conjugation. This is clearly demonstrated, for example, on comparing the ultraviolet spectra of anisole and its complex with aluminium tribromide. The spectrum of anisole changes abruptly on complex formation, and approaches that of benzene. The absorption bands in the region of 219 and 270 nm, attributed[77–80] to conjugation of the lone pair of electrons of the oxygen atom with the system of π-electrons of the ring, disappear on complex formation.

Analogous changes in spectra, indicating breakdown of p_π-conjugation in heteroaromatic compounds on complex formation with aluminium tribromide and with gallium trichloride, have been observed[68] in systems containing phenetole, diphenyl ether, 2-methoxynaphthalene, and their sulphur analogues.

Table 6. Dipole moments μ_c and heats of formation ($-\Delta H$) of complexes in benzene.

Complex	μ_c	$-\Delta H$	Complex	μ_c	$-\Delta H$
$AlBr_3$.D, where D =			$(C_3H_7)_3N$	8.58	33.4
$(C_6H_5)_2O$	7.05	23.2	$(C_5H_{11})_3N$	—	31.5
$(C_3H_7)_2O$	7.26	22.8	$(CH_3)_2NC_6H_{11}$	8.45	32.7
$(C_4H_9)_2O$	7.25	23.2	$C_6H_5N(CH_3)_2$	8.68	24.2
$(C_8H_{17})_2O$	7.41	24.0	$(C_6H_5)_2NCH_3$	8.01	17.2
$C_6H_5OCH_3$	7.00	15.5	C_5H_5N	9.00	31.4
$C_6H_5OC_2H_5$	7.08	16.8	C_9H_7N	9.89	30.1
$(C_6H_5)_2O$	7.29	12.0			
$(p\text{-}CH_3C_6H_5)_2O$	7.58	13.0			
$(p\text{-}BrC_6H_5)_2O$	5.56	9.5	$GaCl_3$.D, where D =		
$\beta\text{-}C_{10}H_7OCH_3$	7.44	15.4	$(C_4H_9)_2O$	6.36	16.0
$\alpha\text{-}C_{10}H_7OC_2H_5$	—	16.1	$(C_8H_{17})_2O$	6.44	17.4
$C_4H_8O_2$	5.40	20.9	$C_6H_5OCH_3$	6.11	10.2
C_4H_8O	7.14	29.4	$C_6H_5OC_2H_5$	—	11.0
$C_5H_{10}O$	7.18	25.6	$(C_6H_5)_2O$	6.30	5.8
$(C_3H_7)_2S$	7.08	17.7	$(C_6H_5)_2S$	7.42	—
$(C_4H_9)_2S$	7.30	17.6	$(C_8H_7)_2S$	—	19.6
$(i\text{-}C_4H_9)_2S$	7.46	18.2	$(C_4H_9)_2S$	7.41	19.0
$(C_5H_{11})_2S$	7.26	18.1	$(C_7H_{15})_2S$	7.83	19.2
$(i\text{-}C_7H_{15})_2S$	8.13	17.1	$(C_5H_{11})_2S$	—	18.3
$(C_8H_{17})_2S$	—	17.1	$C_6H_5SCH_3$	7.39	13.9
$(i\text{-}C_8H_{17})_2S$	—	16.1	$C_6H_5SC_2H_5$	—	15.3
$(C_{18}H_{33})_2S$	7.74	—	$(C_6H_5)_2S$	7.62	11.2
$(C_5H_{11})_2S$	8.24	16.9	C_4H_8S	7.54	18.7
$C_6H_5SCH_3$	7.00	13.1	$(C_3H_7)_3N$	9.01	30.2
$C_6H_5SC_2H_5$	7.14	14.3	$(C_3H_7)_3N$	—	35.2
$(C_6H_5)_2S$	7.55	10.2	$(C_5H_{11})_3N$	9.18	34.9
$C_{10}H_7SC_6H_5$	7.85	9.8	$C_6H_5N(CH_3)_2$	—	24.5
C_4H_8S	—	18.4	$(C_6H_5)_2NCH_3$	—	16.4
$(C_5H_5)_3N$	8.74	31.5			

The destruction of p_π-conjugation in aromatic compounds accompanying complex formation should, of course, be evident in the energetics of the complexing reactions.

Table 6 shows that corresponding complexes with aliphatic and aromatic ethers have closely similar dipole moments. Taking the complexes of aluminium bromide with ethers as example, we can examine the contributions made by the acceptor molecule μ_a and the donor molecule μ_d to the overall dipole moment of the complex μ_c (see scheme at beginning of Section 3). If a tetrahedral conformation is assumed for the bonds about the aluminium atom in the complex, μ_a will be close to the dipole moment of the aluminium–bromine bond. Unfortunately, this quantity is unknown, but it can obviously be assumed, to an adequate degree of approximation, to be the same in all complexes of aluminium bromide with ethers.

The dipole moments of aliphatic and aromatic (unsubstituted) ethers are closely similar at 1.15–1.30 D.[9] The angle α can also be regarded as the same in all these complexes. It therefore follows from the equality of μ_c for complexes of aluminium bromide with aliphatic and with aromatic ethers that the dipole moments of the donor–acceptor bonds μ_{da} are also equal in these complexes.

It has been shown above that there is direct proportionality between μ_{da}/er and ΔH for complexes of donor–acceptor type. Consequently the equality of values of μ_{da} in complexes formed by aluminium tribromide with aliphatic and with aromatic ethers should imply equality of the formation enthalpies of the intermolecular bonds in these complexes.

The total heat of complex formation in an inert solvent can be represented by three components:

$$\Delta H = \Delta H_{da} + \Delta H_a + \Delta H_d$$

where ΔH_{da} is the heat of formation of the donor–acceptor bond and ΔH_d and ΔH_a are the energies or rearrangement of donor and acceptor molecules on complex formation. In the complexes of aluminium bromide with ethers the term ΔH_a can be regarded as constant. Hence in the series of complexes of aluminium bromide with aromatic and aliphatic ethers the quantity $\Delta H_{da} + \Delta H_a$ is the same, and differences in the experimental heats of complex formation ΔH are determined by the term ΔH_d, the energy of rearrangement of the donor molecule. No substantial quantity of heat—of the order of 0.3 kcal mole^{-1} [40]—is required for the molecular rearrangement of aliphatic ethers on complex formation. Therefore the differences in the values of ΔH for complexes of aluminium bromide with aliphatic and aromatic ethers (Table 6) can be ascribed to the energy of rearrangement of the corresponding aromatic ethers.

It has been established spectroscopically[68,74,76] that the rearrangement of aromatic ethers accompanying complex formation consists in the disruption of p_π-conjugation, so that the energy of rearrangement of an aromatic donor is the p_π-conjugation energy. The latter has been determined[68,75] as the difference between the mean value of ΔH for complexes of aluminium bromide with aliphatic ethers (23.3 kcal mole^{-1}) and the corresponding values of ΔH for its complexes with aromatic ethers.

An analogous analysis of the ultraviolet spectra, dipole moments, and heats of formation of complexes with sulphides and amines, as well as of the aluminium chloride, gallium chloride, and boron fluoride complexes with aliphatic and aromatic amines, ethers, and sulphides, has enabled the energies of conjugation E_j in the corresponding molecules to be determined. The accuracy of the determination is 0.8–1.0 kcal mole^{-1}.

Table 7 gives values of E_j found[68] by the method of complex formation with various acceptors. It is seen that closely similar values of the p_π-conjugation energy are obtained for the same donor by complex formation with four different acceptors. The slight discrepancy of 1–1.5 kcal mole^{-1} is primarily due to the steric factor. Among the acceptors investigated the steric effect is least in the aluminium bromide complexes, and greatest in the complexes of boron trifluoride. The most reliable values of E_j are those obtained in the aluminium bromide complexes.

Table 7. Energies of p_π-conjugation (E_j, kcal mole^{-1}) in aromatic ethers, sulphides, and amines obtained by complex formation with various acceptors.

Donor	Acceptor			
	$AlBr_3$	$AlCl_3$	$GaCl_3$	BF_3
$C_6H_5OCH_3$	7.8	7.3	6.5	8.3
$C_6H_5OC_2H_5$	6.5	—	5.7	8.3
$(C_6H_5)_2O$	11.3	11.2	10.9	—
$(p\text{-}CH_3C_6H_4)_2O$	10.3	—	—	—
$(p\text{-}BrC_6H_4)_2O$	13.8	—	—	—
$\beta\text{-}C_{10}H_7OCH_3$	7.9	—	—	—
$\alpha\text{-}C_{10}H_7OC_2H_5$	7.2	—	—	—
$C_6H_5SCH_3$	4.4	5.3	5.2	—
$C_6H_5SC_2H_5$	3.2	4.8	3.8	—
$(C_6H_5)_2S$	7.3	8.5	7.8	—
$\alpha\text{-}C_{10}H_7SC_6H_5$	7.7	—	—	—
$C_6H_5N(CH_3)_2$	8.1	7.6	9.0	9.7
$(C_6H_5)_2NCH_3$	14.9	14.8	17.0	—

The identical values of E_j obtained in complexes with different acceptors confirm the correctness of the initial premises, and indicate that the direct proportionality established between the degree of charge transfer and the energy of the intermolecular bond is applicable to complexes of halides of Group III elements: i.e. it is actually a general characteristic of donor–acceptor bonds.

Published information on the energy of p_π-conjugation is extremely scanty and contradictory[68]. Values have usually been obtained from the heats of combustion of the compounds. Comparison of E_j for a number of amines, ethers, and sulphides indicates that the heteroatoms are arranged in the sequence—N > O > S—according to their capacity for p_π-conjugation with aromatic systems.

The values found for E_j provide a quantitative explanation of why certain aromatic donors form complexes with some acceptors and not with others (with similar values of the steric factor). It is obvious that, if the energy of formation of an intermolecular bond by a donor with a particular acceptor is less than or similar to the p_π-conjugation energy, no complex is formed.

An excellent illustration of the above is provided by complex formation between boron trifluoride and aromatic ethers. The heat of reaction of boron trifluoride with aliphatic ethers is 10–12 kcal mole^{-1}. The destruction of p_π-conjugation in anisole and phenetole requires 7–8 kcal mole^{-1}, and in diphenyl ether ~ 11 kcal mole^{-1}: with this last compound the heat of reaction should be close to zero. Hence boron trifluoride will give quite stable complexes with anisole and with phenetole, but will not form complexes with diphenyl ether.

This also explains the absence of complexes of type $n\sigma$ between iodine and aromatic amines, ethers, and sulphides, as well as of complexes of tin and titanium tetrachlorides with certain aromatic ethers and sulphides.

This method of determining the energy of p_π-conjugation can probably be applied not only to nitrogen, oxygen, and sulphur compounds but also to aromatic compounds of other elements, as well as for estimating the energy of p_π-d_π bonding in organometallic compounds[81].

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Organomagnesium Compounds and Their Complexes as Polymerisation Initiators

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This the first review devoted specifically to polymerisation processes initiated by organomagnesium compounds. Attention is concentrated mainly on the anionic polymerisation of unsaturated monomers (hydrocarbons, acrylates, nitriles, vinylpyridines, halogeno-derivatives, etc.). The review also includes short sections on the anionic polymerisation of carbonyl derivatives and cyclic monomers, on cationic polymerisation, and on initiating systems of the Ziegler-Natta type. The bibliography contains 215 references.

CONTENTS

I. Introduction	874
II. Anionic polymerisation of unsaturated monomers	874
III. Polymerisation of carbonyl derivatives and cyclic monomers	880
IV. Cationic polymerisation	881
V. Ziegler-Natta initiating systems	881

I. INTRODUCTION

Until quite recently organomagnesium derivatives occupied a very modest position among the organometallic compounds used as initiators for anionic polymerisation. This was due to their relatively low reactivity towards non-polar unsaturated monomers (i.e. hydrocarbons of the vinyl and diene types), on which most of the research on anionic polymerisation was concentrated for a long time. With studies on the anionic polymerisation of polar monomers, organomagnesium initiators have begun to attract substantially more attention, since in these cases they are quite comparable in efficiency with many organic derivatives of the alkali metals. The considerable experimental data which have now accumulated on polymerisations initiated by organomagnesium compounds have not yet been reviewed and we have therefore attempted to fill this gap. Modern ideas on the composition and structure of organomagnesium compounds have been discussed in detail in the recently published reviews by Wakefield[1] and by Ashby[2].

II. ANIONIC POLYMERISATION OF UNSATURATED MONOMERS

Among studies of the polymerisation of anionic systems by organomagnesium compounds and their complexes, investigations on various polar unsaturated monomers are of the greatest interest. These processes are often highly efficient and stereospecific. Non-polar and low-polarity monomers exhibit a very limited tendency to polymerisation in such systems.

1. Hydrocarbons

Gilman[3-5] and Kinney[6] showed that unsaturated hydrocarbons of the ethylene and diene series do not react with organomagnesium compounds under ordinary conditions. Instances of the addition of alkylmagnesium halides to unsaturated hydrocarbons were established by Fuson[7-10] for compounds of the fluorene and fulvene series containing highly reactive double bonds—dibiphenylylene-ethylene, tetraphenylfulvene, etc.

The first results on the polymerisation of unsaturated hydrocarbons in the presence of organomagnesium compounds were obtained by Ziegler[11], who found that solid polymers were formed in C_2H_4–RMgX(or R_2Mg) systems at 100–150°C and pressures from 100 to 1000 atm. Raising the temperature enables several other hydrocarbon monomers to be polymerised with the same initiators. Wang Fo-sung, Dolgoplosk, Erusalimskii, et al.[12-14] have shown that polymerisation of various diene hydrocarbons with initiators of the above type at 90°C and above is feasible, but even under these conditions the rate of polymerisation is low. When isoprene is bulk-polymerised at 90°C with an initiator concentration of about 0.003 M, the rate does not exceed 1% h^{-1}. Still lower rates characterise the polymerisation of butadiene and 2,3-dimethylbutadiene. Kinetic data on the consumption of the initiator have established

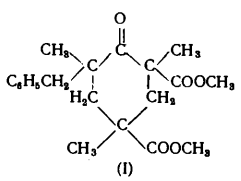
that in the isoprene–$(C_4H_9)_3Mg_2I$ system the rates of initiation and growth are comparable. Thus with an initiator/monomer ratio of 0.01 complete exhaustion of the initiator was observed when 20% of the monomer had been converted. The polyisoprene obtained in the presence of various organomagnesium compounds under these conditions contains 3,4-links as the main structural units (93–99%). The contents of *cis*-1,4-, *trans*-1,4-, and 1,2-links in polybutadiene are 30%, 45%, and 25% respectively (with $(C_4H_9)_3Mg_2I$ as initiator and a polymerisation temperature of 100°C).

Ordinary magnesium alkyls and alkylmagnesium halides are inert towards styrene (at least up to the temperature of its thermal polymerisation). According to Champetier et al.[15] the magnesium–biphenyl–hexametapol [hexamethylphosphoric triamide] system is effective for the polymerisation of styrene and α-methylstyrene.

2. Acrylates and Methacrylates

The ability of organomagnesium compounds to initiate the polymerisation of acrylic esters was discovered by Landler[16] in 1949, but systems of this type began to attract significant attention only from the end of the 1950s. Several publications on this question[11,17–28] deal with the effect of the polymerisation conditions on the microstructure of the resulting polymers. Research has also been done[29–41] on the mechanism and the kinetics of the processes involved.

As in other anionic polymerisations of polar monomers, the processes occurring in these systems are complicated by secondary reactions of the initiator with functional groups in the monomer and the polymer chain. According to Goode[29–32] polymerisation in the methyl methacrylate–phenylmagnesium bromide system at 0°C is accompanied by formation of the compounds



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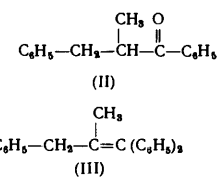

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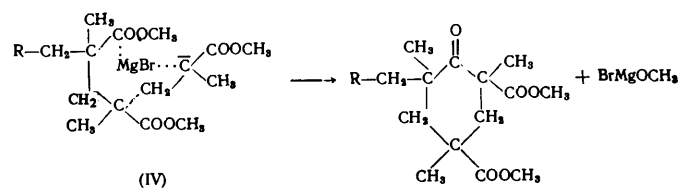
Under the above conditions the relative contents of the polymer and of the compounds (I)–(III) among the reaction products were respectively 96%, 3%, 1%, and 0.1%. Infrared and ultraviolet spectroscopy has established the presence of a large number of short chains in the polymer, the scheme



(IV)

being suggested for their formation.

In a study of the interaction of methyl methacrylate and methyl acrylate with butylmagnesium bromide Tsuruta[33] established that the initiator is consumed mainly in secondary reactions (1,4-addition, interaction with the carbonyl group, metallation with formation of butane)†.

† Similar facts have been established for butyl-lithium, which under similar conditions is consumed predominantly in the formation of butane (55%) and in addition to the carbonyl group (20%)[42].

Studying the kinetics of polymerisation in various organomagnesium halide–methyl methacrylate systems, Watanabe et al.[34–38] and Allen and Moody[39,40] found that the temperature dependence of the rate passes through a maximum, the position of which (the inversion temperature T_i) is determined by the nature of the initiator. In individual cases the reaction orders were also established (Table 1). According to Allen and Moody the inversion phenomenon is due to an increase in the part played by deactivation reactions over a certain temperature range, while the rate of initiation varies little with temperature. Glusker et al.[43–45] have shown that the initiator reacts rapidly with the monomer, but only a small fraction of it forms macromolecules: most of it is consumed in oligomerisation, which is complete after a few minutes, whereas polymerisation lasts under the same conditions for hours. It is suggested that the change which occurs at the inversion temperature in the order of reaction with respect to the monomer (Table 1) represents a change in the way in which the concentration of active centres formed in the initial stage depends on the concentration of the monomer. In this sense the inversion temperature can be regarded as the temperature at which a change occurs in the relative rates of oligomerisation and polymerisation. This ratio in turn determines the fraction of initiator molecules which bring about formation of macromolecules.

Table 1. Kinetics of polymerisation in butylmagnesium bromide–methyl methacrylate systems.

Solvent	Order of reaction with respect to		T, °C	T_i, °C	Ref.
	monomer	initiator			
Toluene	1	2	−50	−25	34, 36
Ether–toluene (1:9)	0.5	—	below T_i	−38.0	40
ditto	2	—	above T_i		40

Table 2. Polymerisation of methyl methacrylate.

Monomer concn., M	Initiator formula	Initiator concn., M	Solvent	T, °C	Mean rate, % min⁻¹	[η]	Polymer structure	Ref.
—	MgR_2	—	–	−40	—	—	isotactic	17
1.00	C_6H_5MgBr	0.333	–	−40	2.6	—	–	54
2.93	$n\text{-}C_4H_9MgBr$	0.200	toluene	−50	0.3	0.247	stereoblock	35
2.93	$Mg(n\text{-}C_4H_9)_2$	0.0005 M	toluene	−78	0.8	2.73	ditto	37
—	$Mg(C_6H_5)_2CO$	0.04	tetrahydrofuran	−70	0.04	—	,,	27
3.3	C_6H_5MgBr	0.14	ether–toluene	−26	—	—	isotactic	39
5.0	C_6H_5MgBr	0.20	ether–toluene	−40	—	—	stereoblock	39

For systems containing ethyl-, phenyl-, and butyl-magnesium bromides the overall activation energy determined below the inversion temperature was 8 ± 0.3, 10 ± 5, and 13 ± 3 kcal mole^{-1} respectively[40]. In various systems of this type the initial rate of polymerisation has been found to depend on the nature of the radical in the organomagnesium compound. When the process is conducted in a 1:9 mixture of diethyl ether and toluene in the presence of various alkylmagnesium bromides, the rate increases in the sequence R = C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_6H_{11}$, C_6H_5, $s\text{-}C_4H_9$.[39] The mechanism of this phenomenon has not been

Table 3. Polymerisation of derivatives of acrylic and methacrylic acids.

Monomer		Initiator		Solvent	T, °C	Mean rate, % min^{-1}	$[\eta]$	Polymer structure	Ref.
type	concn., M	formula	concn., M						
Methyl thiolmethacrylate	0.05	C_6H_5MgBr	0.001	toluene	0	0.7	0.025	stereoregular	55
Ethyl β-*N*-carbazolylmethacrylate	—	C_6H_5MgBr $(C_2H_5)_2NMgBr$	—	ditto	0	0.01	—	ditto	56
Allyl acrylate	—	C_6H_5MgBr	—	» »	—50	—	1.5	crystalline	57
Menthyl methacrylate	3.3	C_6H_5MgBr	0.1	» »	—15	0.15	0.110	stereoregular	58
Ditto	—	C_6H_5MgBr	—	hydrocarbon	—70	—	—	isotactic	59
Methyl α-phenylacrylate	0.02	C_6H_5MgBr	0.0006	toluene	—78	0.005	0.130	–	60
Methyl α-chloroacrylate	0.025	C_6H_5MgBr	0.0005	ditto	room	0.01	0.309	crystalline	61
Methyl α-chlorothiolacrylate	0.025	C_6H_5MgBr	0.0005	» »	—78	0.04	0.047	ditto	61
s-Butyl methacrylate	—	s-C_4H_9MgBr	—	» »	—40	—	0.055	isotactic	62
α-Methylbenzyl methacrylate	—	C_6H_5MgBr	—	hydrocarbon	—70	—	—	isotactic	59
2-Methyl-2-nitropropyl methacrylate	—	C_6H_5MgBr	—	—	—	—	—	isotactic	63
Trimethylsilyl and benzyl acrylates and methacrylates	—	C_6H_5MgBr	—	—	from −70 to −78	—	—	isotactic	64
2,3-Epoxy- and 2,3-epithio-propyl methacrylate*	—	i-C_4H_9MgBr C_6H_5MgBr $C_6H_{11}MgBr$	—	ether toluene tetrahydro-furan	—78	—	—	stereoregular	65

* Polymerisation occurs only at the double bond.

specially investigated, and the observed differences may be attributed to variation in either the initiation rate constant or the fraction of initiator molecules which form active growth centres. The latter hypothesis is the more plausible.

Watanabe et al.[36] have studied the effect of various complexing agents (KA) on the rate of polymerisation in the methyl methacrylate–butylmagnesium bromide system at [A]/[In] ratios up to unity. Among the large number of compounds used, only pyridine, dioxan, diphenylamine, and diethylamine were found to have an activating effect. It is supposed that new, more active organomagnesium compounds are formed.

The polymerisation of acrylic and methacrylic esters with organomagnesium compounds often occurs stereospecifically. The influence of the polymerisation conditions on the character of the polymers and on the rate of the process can be judged from Tables 2 and 3. The mechanism of the formation of stereoregular polymers, suggested by various authors for systems of this type, is discussed in Reich and Schindler's monograph[46]‡. As for other anionic systems, it is assumed that the decisive stage is formation of a coordination complex of the growing chain and the monomer, which in the case of the ester complexes of organomagnesium compounds would involve displacement of the ester by the monomer. Watanabe[37] explains the role of the nature of alkyl and halogen in the organomagnesium compound by their forming part of a gegenion, to which he assigns the formula $[RMg_2X_2]^+$. Roha[47], examining the known experimental facts in terms of the effect of ionic factors on the structure of the chain, notes that organomagnesium initiators exhibit greater stereospecificity§ than do alkali-metal alkyls, and he attributes this to the relatively less ionic character of organomagnesium compounds. The formation of isotactic polymers of higher molecular weight than the atactic polymers, which is noted in several cases, is explained by Goode[29–32] on the assumption that the deactivating reactions limiting the growing chains take place predominantly when the latter are highly ionic in character, i.e. under conditions which do not ensure formation of isotactic polymers.

Study by nuclear magnetic resonance spectra of the effect of the polymerisation temperature on the structure of polyacrylates formed in the presence of phenylmagnesium bromide and diphenylmagnesium has shown[48–53] that the mode of opening of the double bond is determined at the very start of the reaction. Subsequent variation in temperature has no effect on the structure of the polymer.

3. Nitriles

The ability of organomagnesium compounds to add at the double bond of unsaturated nitriles was first established in 1923 for vinylacetonitrile[66,67]. Investigation of the polymerisation of acrylonitrile and methacrylonitrile originated in a paper by Beamen[68] in 1948, which established that it was possible to obtain polymers of low molecular weight by conducting the process in the presence of butylmagnesium bromide in ethereal medium at temperatures between 20° and −75°C. Acrylonitrile polymers of low molecular weight were also obtained by Terent'ev and Kost[69] and by Askarov et al.[70,71] by the action of several other organomagnesium compounds in ethereal[69,70] and hydrocarbon[71] media. The formation of short chains in all these cases was probably due to an unfavourable ratio of monomer and initiator concentrations. As the work of Erusalimskii, Kulevskaya, et al.[72–78] has established, polymers of molecular weight up to 5×10^5 are formed when polymerisation is conducted in organomagnesium halide–acrylonitrile–hydrocarbon systems at −75°C with the ratio $[M]/[In] \simeq 100$, where [M] is the concentration of monomer and [In] the concentration of initiator¶. Study of the mechanism and kinetics of this process, which has been investigated

‡ Some of the papers which we have cited on the mechanism of the polymerisation of methyl methacrylate are considered in greater detail in this monograph.

§ For example, poly(methyl methacrylate) formed under the influence of phenylmagnesium bromide at −20°C comprises 99% of isotactic sequences[28].

¶ The formation of acrylonitrile polymers of high molecular weight by the use of organomagnesium halides has been reported in a patent[79].

in greatest detail in the acrylonitrile–butylmagnesium chloride–toluene system[74-77], shows that only a small fraction (about 0.01) of the initiator molecules form growing chains. A specific deactivation reaction affects only the initiator, and does not extend to active growth centres, as is indicated by several factors consistent with the development of polymerisation through "live" polymers. These results, together with the finding that the reaction was of the first order with respect to the initiator (for the system containing butylmagnesium chloride) and of the second order with respect to the monomer, while the molecular weight of the polymer was independent of the monomer concentration, led to the following scheme for the process

$$\begin{array}{l} \mathrm{In} + \mathrm{M} \rightleftarrows (\mathrm{In}\cdot\mathrm{M}) + \mathrm{M} \overset{K}{\rightleftarrows} (\mathrm{In}\cdot\mathrm{M}_2) \xrightarrow[k_1]{} \mathrm{M}^* \\ \qquad\qquad\qquad\quad \searrow^{k_3} \\ \qquad\qquad\qquad\quad \text{inactive compounds} \\ \mathrm{M} + \mathrm{M}^*_{n-1} \xrightleftharpoons{\text{rapid}} (\mathrm{M}^*_{n-1}\cdot\mathrm{M}) \xrightarrow[k_2]{\text{slow}} \mathrm{M}^*_n \end{array} \qquad (3)$$

In this scheme the intermediate complexes In.M and In.M_2 are formed, K is the equilibrium constant, k_1, k_2, and k_3 are the rate constants of initiation, growth, and deactivation respectively, and M* is an active centre.

It follows from Eqn. (3) that the proportion of the initiator which forms active centres is determined by the ratio of the rates of initiation and deactivation, i.e. $Kk_1[\mathrm{M}]^2/k_3$. This quantity can also be expressed in terms of the ratio of the experimental molecular weight $\bar{M}_{\mathrm{exp}}$ to the theoretical value $\bar{M}_{\mathrm{th}}$ calculated from [M], [In], and the degree of conversion. Hence

$$\frac{Kk_1}{k_3}[\mathrm{M}]^2 = \frac{M_{\mathrm{exp}}}{\bar{M}_{\mathrm{th}}} \quad .$$

It has been shown[74,77] that a linear relation exists between $\bar{M}_{\mathrm{exp}}/\bar{M}_{\mathrm{th}}$ and $[\mathrm{M}]^2$, which supports the suggested scheme.

The same papers[74,77] record peculiarities of the process depending on the nature of the initiator. In particular, the reaction is of the second order with respect to the initiator and of the first order with respect to the monomer when $(C_4H_9)_3Mg_2I$ is used and (unlike the situation with C_4H_9MgCl and $(C_4H_9)_2Mg$) the polymers formed have a relatively wide molecular-weight distribution. This last feature has been interpreted in terms of the presence of different active centres in equilibrium[80]:

$$\mathrm{RMgI} + \mathrm{R_2Mg} \rightleftarrows \mathrm{R{-}Mg}\overset{\mathrm{R}}{\underset{\mathrm{I}}{\diagup\diagdown}}\mathrm{Mg{-}R} \quad .$$

Consistency of this view with experiment has been confirmed by Bresler et al.[81]

The polymerisation of acrylonitrile in hydrocarbon solution, in contrast to other such processes involving "live" polymers, does not go to completion, owing to the insolubility of polyacrylonitrile in such media and the passage of the growing chains into a solid phase which cannot be penetrated by the monomer. The present of "trapped" live chains in such reaction mixtures can be detected if the system is homogenised by means of a suitable solvent, in particular dimethylformamide[80]. In dimethylformamide medium the process goes extraordinarily rapidly, complete conversion of the monomer being easily achieved†. It is interesting that the rate of polymerisation is substantially increased even in the presence of catalytic quantities of dimethylformamide. Interaction of the latter with organomagnesium halides at −75°C produces coordination complexes, which are less subject to deactivation by interaction with acrylonitrile, and ensure the formation of a larger number (in comparison with RMgX) of active centres[77,78]. This constitutes one of the main reasons for the activating effect of dimethylformamide at $[\mathrm{HCON(CH_3)_2}]/[\mathrm{RMgX}]$ ratios of about unity. Catalytic quantities of dimethyl sulphoxide[78] and hexamethylphosphoramide[82] exert an analogous influence on polymerisation in acrylonitrile–organomagnesium halide–toluene systems. Krasnosel'skaya and Erusalimskii[82] have shown that the acceleration of polymerisation in the presence of complexing agents has various causes. Thus catalytic quantities of hexamethylphosphoramide produce only an increase in the number of active centres: a substantial increase in the yield of polymer is not accompanied in this case by change in molecular weight, compared with results obtained under the same conditions in the absence of hexamethylphosphoramide. Dimethyl sulphoxide and dimethylformamide cause an increase in yield and in the molecular weight of the polymer: both the growth rate constant and the number of active centres increase here (Table 4).

Table 4. Polymerisation in systems comprising 1.5 M acrylonitrile + 0.01 M tributyldimagnesium iodide + a complexing agent in toluene[82] at −75°C for 1 min.

Complexing agent	Conversion, %	Mol. wt., $10^{-3}M$	Efficiency of initiation, %
–	11	73	1.3
Hexamethylphosphoramide	65	73	7.7
Dimethylsulphoxide	60	200	2.5
Dimethylformamide	45	160	2.3

Several other papers have discussed the polymerisation of acrylonitrile and methacrylonitrile initiated by organomagnesium compounds as involving the intermediate formation of complexes. Such a conclusion was drawn, for example, by Dawans and Smets[83], who investigated the copolymerisation of acrylonitrile and methacrylonitrile with other monomers under the influence of phenylmagnesium bromide‡, and also by Natta et al.[86], who regard these processes as cases of anionic coordination.

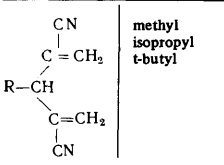
Several papers describe the synthesis of stereoregular polymers of acrylonitrile[87] and methacrylonitrile[86,88-91] under the influence of organomagnesium compounds. In most cases the degree of stereoregularity is estimated from the crystallinity and the solubility of the polymers, but hardly any data are given on their detailed microstructure. This does not apply to work[92-94] in which nuclear magnetic resonance was used to investigate the structure of methacrylonitrile polymers obtained in the presence of various organometallic initiators. The most stereospecific initiators proved to be organomagnesium compounds,

† At −75°C and concentrations of 1.5 M acrylonitrile and 0.005 M butylmagnesium chloride in dimethylformamide medium, polymerisation is complete in a fraction of a minute. In toluene the initial stage of the process (up to 5% conversion) goes at a rate of around 1% min^{-1}.[78,80]

‡ Data on the copolymerisation of acrylonitrile with various monomers in the presence of organomagnesium initiators have been given also in other papers[84,85].

which yielded predominantly isotactic polymers§. According to Natta[86] the stereospecificity of the polymerisation of unsaturated nitriles in the presence of alkylmagnesium halides is due to orientation of the monomer at the stage of coordination of an active centre with the monomer at the nitrogen atom.

Table 5. Polymerisation of α-alkylacrylonitriles and β-alkyl-αγ-dimethyleneglutaronitriles.

Monomer	R	Catalyst	Solvent	Temp., °C	Duration of polymerisation, h	Conversion, %
$CH_2=C(CN)R$	n- propyl	CH_3MgBr	tetrahydrofuran	room	20—70	20
		$Mg(C_2H_5)_2$	toluene	—78		
	isobutyl	CH_3MgBr	tetrahydrofuran	—78	20	10
			toluene			
	neopentyl	CH_3MgBr	tetrahydrofuran	—78	20—70	30
			toluene			
	methyl	CH_3MgBr	toluene	0	4	10
	isopropyl	CH_3MgBr	toluene	0	24	25
	t-butyl	CH_3MgBr	tetrahydrofuran	0	5—25	10
				—78		

The polymerisation of α-alkylacrylonitriles and of β-alkyl-αγ-dimethyleneglutaronitriles under the influence of organomagnesium compounds has been described by Covács and Marvel (Table 5).[96] Furukawa et al.[97] have used phenylmagnesium bromide to initiate the polymerisation of *cis*- and *trans*-crotononitrile.

4. Vinylpyridines

The polymerisation of vinylpyridines in the presence of organomagnesium compounds, studied mainly by Natta[98-102], is interesting in connection with the role of various factors in producing the chain structure. In the polymerisation of 2-vinylpyridine in hydrocarbon medium by various metal alkyls, only the magnesium derivatives (RMgX, R_2Mg, R_2NMgX) exhibit high stereospecificity. Nuclear magnetic resonance data indicate that the polymers have an isotactic structure[103-105]. Views on the mechanism of stereoregulation are based on the considerations formulated in discussing the polymerisation of unsaturated nitriles[86] (see subsection 3). In the present case it is postulated that the heteroatom and the double bond of the monomer take part simultaneously in acts of complex formation. This is consistent with differences in the behaviour of 2- and 4-vinylpyridines: stereoregular polymers are formed only in the former case. In Natta's opinion, considerable remoteness of the nitrogen atom from the vinyl group eliminates the possibility that complexes of the growing chain can be formed by means of both donor positions in the monomer, and thereby excludes its rigid orientation in acts of growth. The role of complex formation as a factor determining the microstructure of the polymer is clearly exhibited in the polymerisation of 2-vinylpyridine in the presence of catalytic quantities of Lewis bases, which either hinder or eliminate (depending on their relative basic strength) the stage of complex formation between the growing chain and the monomer (Table 6).

Data are lacking on the kinetics of polymerisation in these systems. The papers cited above indicate only the total conversion of the monomer achieved after a standard time. As Fontanille and Sigwalt[15] remark, polymerisation in the 2-vinylpyridine–biphenyl–magnesium–hexametapol system involves "live" chains and is characterised by a high growth rate constant.

Table 6. Polymerisation of 2-vinylpyridine in anionic systems in toluene at 45°C.[102].

Initiator	Complexing agent (CA)		Yield of polymer in 5 h, %	Crystalline fraction	
	compound	molar ratio [CA]/[In]		content, %	[η] *
$(C_6H_5)_2Mg$	—	—	96	93	0.34
$(C_6H_5)_3MgBr$	—	—	96	85	0.30
C_6H_5MgBr	—	—	92	98	0.49
C_6H_5MgBr	pyridine	2.5	45	0	—
C_6H_5MgBr	diethyl ether	4	80	38	—
C_4H_9Li	—	—	98	0	—
$C_8H_{17}Na$	—	—	85	0	—
$(C_2H_5)_2Be$	—	—	97	**	—
$(C_2H_5)_3Al$	—	—	0	—	—
$[(CH_3)_2N]_2Be$	—	—	40	40	0.27
$[(CH_3)_2N]_3Al$	—	—	15	85	0.35
$LiAlH_4$	—	—	98	82	—

* Determined in dimethylformamide at 30°C.

** Polymer contains 65% of a fraction insoluble in boiling acetone and characterised by low crystallinity.

Some idea of the rate of polymerisation of 2-vinylpyridine with organomagnesium initiators is given by Erusalimskii and Ovsyannikov's results[106] for tributyldimagnesium iodide. At monomer and initiator concentrations of 2.0 M and 0.1 M respectively, quantitative conversion in toluene is reached at −20°C in 10 min. It is shown that effective polymerisation is possible at −50°C. The same paper reports that in hydrocarbon medium 2-methyl-5-vinylpyridine undergoes polymerisation at room temperature.

5. Chlorine-containing Monomers

Organomagnesium compounds have been used for the polymerisation of chlorine-containing monomers—vinyl chloride[107-111], vinylidene chloride[112], chloroprene[14,113-115], and 2,3-dichlorobutadiene[116]—in several researches. Deactivation plays an especially important part with most of these monomers, this being due not only to the great tendency of chlorine atoms to enter into side-reactions with metal alkyls. The low relative activity of these monomers in anionic polymerisation eliminates the possibility of conducting the process at low temperatures; even at room temperature they do not polymerise very rapidly in anionic systems. This makes it impossible to suppress side-reactions by substantially lowering the temperature¶.

§ No data are yet available on the structure of polyacrylonitrile formed in systems involving organomagnesium compounds. A stereoblock isosyndiotactic structure (1 : 1) has been established[95] for the polymer produced in the acrylonitrile–butyl-lithium–toluene system at −78°C.

¶ For example, effective polymerisation can be accomplished in the butyl-lithium–methyl methacrylate system only because the monomer is sufficiently active in the growth reaction at low temperatures. Even at −30°C polymerisation is effectively suppressed by reactions at the carbonyl group.

The polymerisation of vinyl chloride, vinylidene chloride, and chloroprene initiated by organomagnesium compounds is characterised by low consumption of the initiator in forming active centres and cessation of the process at a low degree of conversion. The latter feature, which is shown also by polymerisation of the same monomers in the presence of lithium alkyls[115,117,118], is due to the extension of deactivating reactions to the growing chains. The mechanism of these reactions probably consists in detachment of chlorine from the end of the growing chain by a gegenion:

$$\sim CHCl-CH_2^- \quad MgX \rightarrow \sim CH=CH_2 + MgClX$$

This is supported by the data of Guyot and Pham Quang Tho[108-111], who detected vinyl groups in the polymer formed in the vinyl chloride–t-butylmagnesium chloride–tetrahydrofuran system. These workers established the slowness of initiation, which under their conditions lasted for practically the whole time of polymerisation[111], and also the incomplete consumption of the initiator by the initiation reaction: ~ 75% of the initial quantity of initiator was deactivated[110,111]. Polymerisation in this system was found to be formally similar to radical polymerisation (microwave resonance of the polymers constant with time, steady-state occurrence of the reaction). Nevertheless, in view of all the experimental results obtained, the authors do not doubt the anionic character of the polymerisation they were studying.

The occurrence of secondary reactions between the organomagnesium initiator and the chlorine-containing monomer is shown by Erusalimskii and Krasnosel'skaya's investigation[114,115] of polymerisation in the chloroprene–tributyldimagnesium iodide–heptane system. Data on the kinetics of polymerisation, the consumption of the initiator, and the variation in the total concentration of organomagnesium compounds indicate the rapid occurrence of the following parallel reactions

$$M + In \begin{cases} \rightarrow \text{initiation} & < 1\% & (4) \\ \rightarrow \text{elimination of Cl (formation of MgClX)} & 8\% & (5) \\ \rightarrow \text{formation of inactive organomagnesium compounds} & \sim 91\% . & (6) \end{cases}$$

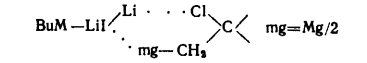
Polymerisation in this system is of the first order with respect to monomer and initiator, and is described by the general equation

$$\frac{[M]_0 - [M]}{[M]_0} = 1 - e^{-k_2/k_3[M^*]_0 (1-e^{-k_3})}\dagger$$

where $[M]_0$ and $[M^*]_0$ are the concentrations of monomer and active centres at zero time, and k_2 and k_3 are the growth and termination rate constants. Values of k_2 and k_3 calculated by means of this equation for 25°C are respectively 0.016 M^{-1} s^{-1} and 1.3×10^{-5} s^{-1}.

A general idea of the effectiveness of the anionic polymerisation of monomers of this type is given by the limiting conversion attainable in several cases (Table 7).

Initiating systems which are considerably more effective towards these monomers are formed by the interaction of certain organomagnesium and organolithium compounds, and have been suggested by Krasnosel'skaya for the polymerisation of chloroprene[112,119-121], vinyl chloride[112,120], and vinylidene chloride[112]. In particular, the interaction of tributyldimagnesium iodide and butyl-lithium in the proportions 1 : 2 in hydrocarbon medium at room temperature yields the heterogeneous system $C_4H_9Li.LiI$ (solid phase)–$2(C_4H_9)_2Mg$ (in solution). The components of the system, which can be easily separated from one another, exhibit enhanced activity towards polymerisation only when present together. Under conditions comparable with those in Table 7 this system brings about up to 90% conversion of chloroprene and up to 50% conversion of vinyl chloride at room temperature. Increased efficiency has been noted also for vinylidene chloride; in this case the limiting conversion was not established. Analogous phenomena are observed when systems formed by the direct interaction of dibutylmagnesium with the complex $C_4H_9Li.LiI$ are used[121]. The hypothetical structure



has been suggested[121] for the active centres.

Table 7. Limiting conversion in the anionic polymerisation of unsaturated chlorine-containing monomers.

Monomer		Initiator		Solvent	Initial rate of polymerisation, % h^{-1}	T, °C	Limiting conversion,		Ref.
compound	concn., M	formula	concn., M				%	reached in, h	
Vinyl chloride	8.0	BuLi	0.09	heptane	3	25	25	15	112
ditto	3.6	Bu^tMgCl $BuMgCl$	0.156	tetrahydrofuran	8	25	~50	25	108, 109
Vinylidene chloride	2.0	Bu_3Mg_2I	0.045	heptane	1	20	18	20	112
		BuLi	0.03	heptane	1	20	4	10	112
ditto	2.0	BuLi	0.10	heptane	1.5	25	7	24	115
Chloroprene	6.0								
ditto	6.0	Bu_3Mg_2I	0.08	heptane	4	40	50	50	115

The mechanism of the process has been examined in greater detail on the closely similar system $C_4H_9Li.LiI$–C_4H_9Li. According to results for the polymerisation of vinyl chloride obtained by Gasan-Zade and Mazurek[112], the enhanced efficiency of the process is due to an increase in the effectiveness of initiation and also a more favourable k_2/k_3 ratio for growth. Both of these constants have lower absolute values than in the polymerisation of vinyl chloride by butyl-lithium.

Dichlorobutadiene differs fundamentally in behaviour from the above monomers. Polymerisation in the $C_4H_4Cl_2$–$(C_4H_9)_3Mg_2I$ system at 20°C takes place at a relatively high rate (around 10% h^{-1} with [M] = 2 M and [In] = 0.025 M), and can be brought to high degrees of conversion[116]. This interesting feature, indicating the exceptionally minor role of termination reactions, can be explained by enhanced reactivity of the monomer (i.e. increase in k_2) or by the absence of labile chlorine atoms (1,2-units) in the polymer chain. In polymers of chloroprene formed by the action of metal alkyls the presence of such units (together with the main structural *trans*-1,4-units) is not excluded[114].

6. Other Monomers and Certain Special Cases

Several other anionic systems involving organomagnesium compounds are worthy of attention. Thus in the

† Reactions (4)–(6) are disregarded here, since they are complete at the very first stage, and the overall rate of polymerisation is low. The value of $[M^*]_0$ is determined from data on the degree of polymerisation, since $\bar{P} = x[M]_0/[M^*]_0$, where x is the conversion.

vinyldiphenylphosphine oxide–organomagnesium halide–toluene system[123] it has been established that termination reactions do not occur (at 25°C). It has been concluded from colorimetric measurements that initiation involves intermediate formation of a monomer–initiator complex, which is then converted into a coloured monomeric anion. An analogous mechanism is assumed for growth (coordination of the phosphine oxide group of the monomer with an active centre).

An interesting case of the use of organomagnesium compounds for synthesising anionic initiators of high molecular weight, suitable for the preparation of graft polymers, has been described by Guber and Egle[124]. Interaction of a styrene–acrylonitrile copolymer with dimethylsilylmethylmagnesium chloride in tetrahydrofuran forms magnesium-substituted imino-groups on the polymer chain:

$$\sim CH_2CH(C_6H_5)-CH_2CH(CN)\sim \xrightarrow{RMgX} \sim CH_2CH(C_6H_5)-CH_2CH(RC{=}NMgX)\sim ,$$

At temperatures of −30°C and below these addition products effectively polymerise acrylonitrile, methyl methacrylate, and 4-vinylpyridine to give the corresponding hybrid polymers.

Grignard reagents have been used by Japanese workers for the migration polymerisation of acrylamide[125–127]. Phenylmagnesium bromide in dioxan showed the highest activity. The peculiar mechanism of this process, leading to the formation of poly-β-alanine, has been studied by Nakayama et al.[126,127]. In particular, when polymerisation is conducted at a high temperature (100°C)‡ in toluene and in pyridine, appreciable differences are observed depending on the nature of the solvent: in pyridine a considerable quantity of dimer is formed, which is barely noticeable in toluene. It has therefore been suggested that polymerisation has a stepwise mechanism in pyridine and a chain mechanism in toluene. The synthesis of block copolymers of acrylamide with acrylonitrile and caprolactam under the influence of alkylmagnesium halides has been reported[128].

Among other monomers which can be polymerised by means of organomagnesium initiators are isopropyl crotonate[129,130], t-butyl crotonate[129–131], methyl atropate[132], isopropenylpyridine[133], and penta-2,4-dienonitrile[134].

III. POLYMERISATION OF CARBONYL DERIVATIVES AND CYCLIC MONOMERS

During recent years organomagnesium compounds have been tested as initiators for the polymerisation of a large number of aldehydes and ketones. Attention has been concentrated mainly on the structure of the polymers formed; in several cases the action of the organomagnesium compounds has been found to be stereospecific (Table 8). Hardly any work has been done specifically on the mechanism of the polymerisation of monomers of this type initiated by organomagnesium compounds. The well known concepts relating to aldehyde–metal alkyl systems, formulated by Natta[136] and by Furukawa[137,138], and generalised by Vogl[154], are entirely applicable to these systems. A case of particular interest is the interaction of but-3-en-2-one and of 3-methylbut-3-en-2-one with butylmagnesium bromide in ethereal solution and in hexane. It was established that polymerisation and secondary reactions—dimerisation of the monomer and formation of butane—take place in parallel[33].

‡ Lowering the temperature for the anionic polymerisation of acrylamide diminishes the role of migration effects. It is possible that polyacrylamide completely free from isomerised units may be synthesised by anionic initiation, but this has not yet been established experimentally.

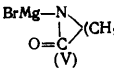
Most of the papers on the polymerisation of various cyclic monomers by the compounds RMgX and R_2Mg are similarly purely descriptive in character. They are concerned predominantly with ethylene and propylene oxides[155–162], with which the process goes efficiently to form polymers of high molecular weight; the oxides of butadiene[157] and of styrene[157], epichlorohydrin[157], and epoxyalkyl ethers[163] have also been mentioned. In the presence of a Grignard reagent trimethylene sulphide yields a crystalline polymer[164]. Organomagnesium compounds initiate the polymerisation of epoxyorganosilanes[165]. Data have been published on the synthesis of copolymers of oxides with other monomers[166], in particular with phthalic anhydride.

Table 8. Polymerisation of aldehydes, ketones, and dimethylketen.

Monomer	Initiator	Solvent	T, °C	Duration	Yield of polymer %	State of polymer	Ref.
HCHO	EtMgBr	Et_2O	−78	—	—	solid	135
CH_3CHO	RMgX	—	−70	—	—	crystalline	136
CH_3CHO	EtMgBr	hexane	−78	20 h	26	ditto	138
$CH_3CH_2CH_2CHO$	Et — and BuMgBr	heptane	−78	—	25—30	"	139
$CH_3CH_2CH_2CHO$	CH_3 — and C_6H_5MgBr	$(CH_3)_2O$	−75	10 min	95—97	"	140
$CH_3CH_2CH_2CHO$	Et_2NMgBr	Et_2O	—	—	40	—	141
CH_2ClCHO	Et_2Mg	toluene	−78	3 days	8	—	142
CH_2=CHCHO	RMgBr	Et_2O, ether hexane,	20—50	5—36 h	10—30	mixture of liquid and solid	143
CH_2=CHCHO	n-C_4H_9MgBr	toluene	room	24 h	30	solid	144
But-3-en-2-one, 1-phenylprop-2-enone, 3-methylbut-3-en-2-one	C_6H_5MgBr; Et_2Mg	in bulk	0	—	—	crystalline	145—147
4,4-Dimethylpent-1-en-3-one	RMgX	tetrahydrofuran	—	—	—	amorphous	148
Acetophenone	C_6H_5MgBr	toluene	−78	3 days	90	solid	149
Dimethylketen	R_2MgX; R_2Mg	toluene, tetrahydrofuran, etc	from 20 to 78	—	20	—	150—153

In most cases the processes can be assumed to have a mechanism of anionic coordination. A possible exception is provided by the initiating systems $RMgX–H_2O$, described by Vandenberg[157], which, by analogy with $R_3Al–H_2O$ systems, can be regarded as cationic. The polymerisation of ethylene and propylene oxides under the influence of R_2Mg has been investigated in rather more detail. According to Kagiya et al.[158–161] this process, in which polymers of high molecular weight are formed in good yield, has a termination reaction. The activation energies for the reactions of growth and termination are found to be 15.8 and 29.2 kcal mole^{-1} respectively.

Organomagnesium compounds, free from ether, are able to initiate the polymerisation of caprolactam[167]. The first act—addition of alkylmagnesium halide to the monomer—takes place even at room temperature, with formation of the compound



(V)

The development of polymerisation requires a substantially higher temperature, 240–250°C. According to the patent literature[168,169] caprolactam is effectively polymerised by the action of organomagnesium compounds in the presence

of certain promoters, e.g. *N*-acetylcaprolactam and *N*-phenylsuccinimide. These agents probably add to the product (V) to form centres which are more active for polymerisation. According to Vofsi et al.[170] the rate constants of reactions of this type are several orders of magnitude larger for substituted than for unsubstituted lactams (Table 9).

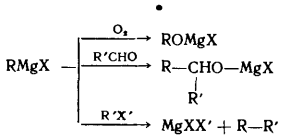
Table 9. Interaction of pyrrolidones with pyrrolidonylmagnesium bromide in tetrahydrofuran at 25°C.[170]

Lactam	Addition rate constant, 10^2 M^{-1} s^{-1}
Pyrrolidone	$3 \cdot 10^{-7}$
N-Methylpyrrolidone	$5 \cdot 10^{-2}$
N-Acetylpyrrolidone	2.8
N-Benzoylpyrrolidone	9.5

Promoter–RMgX systems are used also for initiating the copolymerisation of caprolactam with pyrrolidone[171] and with acrylamide[172]. β-Propiolactone also polymerises in the presence of organomagnesium initiators[173].

IV. CATIONIC POLYMERISATION

Organomagnesium halides, which are Lewis acids, can in principle be regarded as cationic agents. Their ability to initiate cationic polymerisation was discovered with vinyl ethers; here there is no doubt about the mechanism of the process, in view of the inertness of these monomers towards anionic initiators. The first observations in this field were made by Cray[174], who established that various vinyl ethers underwent polymerisation in bulk and in solution in the presence of butylmagnesium bromide at 80°C. It has been assumed that polymerisation is effected by MgX^+, RMg^+, or Mg^{2+} ions, with the monomer acting as cocatalyst. By analogy with other cationic systems it is more probable that catalytic complexes are formed, and produce carbonium ions (if the monomer does actually function as a cocatalyst). However, the concept of the cocatalytic action of vinyl ethers in cationic polymerisation, which was generally accepted until quite recently, requires re-examination in view of results obtained by Eley and Johnson[175], who established that hept-1-en-3-one is inert towards boron trifluoride in hydrocarbon medium provided that the system has been carefully freed from traces of moisture. There is no direct evidence of this kind for organomagnesium initiators, but Iwasaki et al.[176] consider that the presence of an independent cocatalyst is essential in vinyl ether–organomagnesium halide systems. They include among such agents oxygen, aldehydes, metal oxides, and halogenated hydrocarbons. In their opinion reactive compounds can result from the reactions



The cocatalytic action of these agents is confirmed by the results[176]. A positive effect due to oxygen has been noted also by Bruce and Farren[177], but the suggested interpretation of these phenomena cannot be regarded as reliable. In particular, formation of catalytic complexes of the type $R^+[RMgX_2]^-$ cannot be excluded in the presence of alkyl halides. Furthermore, Iwasaki et al.[176] distinguished between use of the $RMgX-O_2$ system and that of alkoxides ROMgX for initiating the polymerisation of vinyl ethers. Only in the former case are polymers of high molecular weight produced. Consequently the active centres which appear when both RMgX and oxygen are present are more complicated in character. As with most other cationic systems, results obtained with maximum exclusion of traces of water would probably be of great interest.

V. ZIEGLER–NATTA INITIATING SYSTEMS

Ziegler's early patents[11] already included the use of organomagnesium compounds among other organometallic components for synthesising new complex catalysts. These compounds have since been used in systems of similar type for the polymerisation of alkenes[13,178–185], acetylene and phenylacetylene[186,187], styrene[13,188–190], and dienes[13,185,191–201]. These systems have not found wide application, obviously owing to their being less stereospecific than catalysts based on aluminium derivatives. In the polymerisation of propene under the influence of $RM-TiCl_3$ catalytic systems, according to Natta[202], organomagnesium compounds result in the formation of polymers having a rather lower isotactic fraction (up to 85%) than do organoaluminium and organoberyllium compounds (90% and 96% respectively). In the polymerisation of diene hydrocarbons a highly stereospecific process is achieved with $RMgX-TiCl_4$(or $TiBr_4$) systems only when certain third components—alkyl iodides[203], hydrogen iodide[204], lithium iodide[205], and others[206–208]—are also present. Under these conditions polybutadiene containing up to 98% of *cis*-1,4-units can be synthesised. In the absence of such additional agents, the greatest homogeneity of chain structure in the polymerisation of dienes under the influence of titanium–magnesium complexes has been found in the isoprene–$(C_4H_9)_3Mg_2I$–$TiCl_4$ system. With an initial ratio of Mg/Ti = 1.5, the polyisoprene formed contained 84% of *cis*-1,4-units[13]. *cis*-1,4-Polybutadiene has been obtained in high yield by using the catalytic system $C_6H_5MgX-TiI_4$ (Mg : Ti ≥ 2).[209]

Ziegler–Natta catalysts including magnesium components have been used for the polymerisation of various polar monomers, such as vinyl chloride, acrylonitrile, methyl methacrylate, etc.[11,193,194,210]. The mechanism of the polymerisation of polar monomers initiated by Ziegler–Natta catalysts is a matter of controversy. The most plausible view is the free-radical nature of the process. This was first put forward by Furukawa[211] on the basis of results for the copolymerisation of various pairs of monomers; it has since been confirmed in several kinetic investigations[212,213]§. These conclusions, reached in the study of other systems, can probably be extended to systems involving organomagnesium compounds.

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The most interesting aspect of an analysis of the information surveyed in the present Review is to reveal the specific character of organomagnesium compounds distinguishing

§ Milovskaya[214] has discussed a possible mechanism for the generation of free radicals in systems comprising a polar monomer and a Ziegler–Natta catalyst.

them from other organometallic initiators of polymerisation. The data on the polymerisation of isoprene, methacrylonitrile, and 2-vinylpyridine are noteworthy in this connection. In the first case, compounds RMgX and R_2Mg yield polymers constructed almost entirely of 3,4-units (in contrast to the polyisoprene formed by the action of other metal alkyls). In the other two cases a substantially higher stereospecificity of action has been established for these reagents. These characteristics are most probably due to steric factors associated with active centres in the corresponding systems, not to the degree of polarity of the carbon–magnesium bond in the organomagnesium compounds.

Owing to the great sparsity of quantitative data it is difficult to draw rigorous conclusions on the reactivities of different organometallic compounds in polymerisation processes, or to establish the place occupied in this sequence by magnesium derivatives. Nevertheless, there are facts indicating divergence from rules to be expected from general considerations. This applies to differences in the behaviour of lithium and magnesium alkyls towards unsaturated hydrocarbons and halogenated monomers, as is shown especially clearly by a comparison of data on the polymerisation of styrene and of vinyl chloride. Thus the growth rate constants in the polymerisation of styrene in hexane (at 30°C)[215] and of vinyl chloride in heptane (25°C)[117] in the presence of butyl-lithium are respectively 5.0 and 0.0099 $M^{-1}\ s^{-1}$. The reactivity of organomagnesium compounds in these systems is opposite in character: they are inert towards styrene, but cause the polymerisation of vinyl chloride.

Finally, it is worth noting that the lower reactivity in acts of initiation and growth, which is usual for organomagnesium compounds (in comparison with alkali-metal alkyls), is accompanied by a relatively lower tendency to undergo various deactivating reactions. In certain cases this will lead to a relation between the rate constants of the elementary reactions which is more favourable to polymerisation than when alkyl derivatives of the alkali metals are used. This is probably the explanation of the substantially higher conversion limit attainable with organomagnesium initiators, compared with organolithium compounds, in the polymerisation of unsaturated chlorinated monomers.

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Dependence of Thermal Stability of Polymers on Their Chemical Structure

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It is shown, on the basis of a large amount of experimental work, how the thermal stability of polymers depends on the strength of the bonds between the atoms forming the macromolecule, on the structure of the chain unit in the macromolecule, and also on the structure of the polymer molecule itself as a whole. Especially detailed attention is given to the effect on thermal stability of such structural features of the chain unit as the presence of side-chains, halogen atoms, and other elements (boron, silicon, phosphorus, various metals), the positions and number of these substituents, and also groups of aromatic character, including benzene rings and various heterocycles. Those structural features which tend to increase the thermal stability of polymers are elucidated.
An important place in the review is occupied by examining the dependence of thermal stability on such structural aspects of the macromolecule itself as the regularity in the arrangement of monomer units along its chain, the isomerism of substitution in the aromatic ring, the presence of branching and cross-linking, copolymerisation, and also the nature of end-groups, etc. A list of 100 references is given.

CONTENTS

I. Introduction 885
II. Strength of bonds between atoms in the macromolecule 886
III. Dependence of thermal stability on structure of chain unit 887
IV. Dependence of thermal stability on structure of macromolecule 901
1. Dependence of thermal stability on regularity of structure of macromolecule 901
2. Effect of isomerism of substitution in the aromatic ring 901
3. Effect of lateral groups and branching 901
4. Dependence of thermal stability on degree of cross-linking of polymer 902
5. Effect of copolymerisation 904
6. Effect of other structural features on thermal stability 904

I. INTRODUCTION

The most important problem of polymer chemistry is to establish the relation between the properties of polymers and their structure. Only when this is known is it possible to solve consciously and successfully the problems involved in preparing polymers having required properties which have been specified in advance.

Although relatively little experimental work has yet been done on the relations between the structure and the properties of polymers, it is already possible, on the basis of known data, to establish certain relations of this type. The main method for finding links between the structure and the properties of polymers is to study and compare the behaviour of series of polymers of analogous structure[1].

We shall not deal here with one extremely important aspect of this problem—the influence of the physical structure of polymers on their properties—which has been determined by the work of Kargin[2]. He has shown, on the basis of a large number of experimental results, that the physical structure of a polymer affects not only its strength but also several of its chemical reactions.

Without being concerned with the whole problem of the relation between structure and properties, we shall examine only its purely chemical aspect. The aim of the present review is to show quite clearly the relations which have now been elucidated between the chemical structure and the thermal stability of polymers, these being of interest in particular in connection with the problem of producing the heat-resistant materials which are so necessary for modern technology.

Let us first define the concepts of heat-resistance and thermal stability, with which we shall often be dealing. *Heat-resistance* we shall take to mean the limiting temperature at which a given polymer is able to maintain a particular mechanical strength. *Thermal stability* will imply the limiting temperature which a given polymer can withstand without chemical change. Above this temperature the polymer begins to undergo chemical breakdown, in most cases accompanied by loss of mechanical strength.

We shall not be concerned here with problems associated with the thermal breakdown of polymers under the simultaneous influence of high temperatures and chemical reagents such as oxygen, water, etc., i.e. the oxidative thermal degradation and the hydrolytic cleavage of polymers.

Various methods are used to assess the thermal stability of polymers. The most widely used are methods of *dynamic thermogravimetric analysis*, in which loss in weight is determined while the temperature is raised continuously and uniformly. *Isothermal thermogravimetric analysis* is often employed also, this being conducted at a constant temperature. These methods are of value only for the preliminary assessment of polymers under laboratory conditions. A more exact estimate of the thermal stability of polymers necessitates prolonged tests at the required temperatures. Methods of determining thermal stability from the loss in weight of polymers on heating has the disadvantage that they give no information on chemical changes unaccompanied by loss of volatile products. In many cases, however, comparative results of the thermogravimetric analysis of various polymers nevertheless give an idea of their thermal stability.

When discussing the dependence of the thermal stability of polymers on their chemical structure, we understand by the latter both the composition of the polymer and various structural features of its chain unit, the individual macromolecule, and the union of individual linear macromolecules joined by chemical bonds. Only a few experimental data have been published on this question, and attempts have been made at certain generalisations in individual reviews [3-8] and monographs [9,10].

The thermal stability of a polymer depends primarily on the strength of the bonds between the individual atoms and groups forming this macromolecule. The strength of these bonds determines the temperature at which they are ruptured as a result of dissociation or other chemical reactions caused by high temperature or various chemical agents. We shall therefore first examine the dependence of the strength of these bonds on the nature of the atoms constituting the polymer macromolecule, and then elucidate the effect on the thermal stability of the polymer of the chemical structure of the chain units and of the macromolecule as a whole.

II. STRENGTH OF BONDS BETWEEN ATOMS IN THE MACROMOLECULE

The strength of a chemical bond depends on the nature of the atoms between which it is formed, the sequence of bonded atoms, the nature of substituents, and other structural features. The strength of bonds can be characterised by the bond energy, which corresponds to the energy of their dissociation into free radicals (Table 1).

Table 1 shows that the most stable bonds are those between carbon atoms. The strength of a bond between atoms of other elements is considerably less. Therefore only those elements in which the energy of the bonds linking one atom to another is sufficiently large are able to form homochain polymers. If, however, the energies of bonds between atoms of elements are small, the polymers show poor stability; and at bond energies less than 37 kcal mole^{-1} elements are completely unable to form polymeric chains, since the latter would obviously break down as a result of thermal degradation even at ordinary temperatures.

The existence of a large number of carbon-chain polymers is due to the high bond energy between carbon atoms. Thus in this case the effect of strength of bonding on the properties of a polymer is shown quite clearly.

Heterochain polymers, whose macromolecules are formed from different elements, show considerably higher bond energies between the atoms (Table 2), so that a marked increase in their thermal stability is observed. Table 2 shows that the energies of bonds between atoms of different chain-forming elements, which are typical of heterochain polymers, are quite high, in many cases exceeding the bond energies encountered in homochain polymers. The highest energies are exhibited by boron–nitrogen and boron–oxygen bonds, and also by those between aromatic carbon and nitrogen or oxygen. The silicon–oxygen bond is also extremely stable. These are the bonds which occur in polymers having the greatest thermal stability.

Table 1. Energy of bonds (kcal mole^{-1}) between atoms of elements [11,12].

Bond	Energy	Bond	Energy
C_{arom}–C_{arom}	98.0	Te—Te	49.0
C_{aliph}–C_{aliph}	83.0	Sb—Sb	42.0
S—S	63.0	Ge—Ge	39.2
Si—Si	53.0	As—As	39.0
P—P	53.0	N—N	37.0
Se—Se	50.0	O—O	34.0

Table 2. Bond energies (kcal mole^{-1}) between atoms of different elements capable of forming heterochain polymers [11,13].

Bond	Energy	Bond	Energy
B_{arom}—N_{arom}	115.0	C_{aliph}—N^{III}	82.0
B—O	113.5	P^{III}—O	81.7
C_{arom}—N^{III}	110.0	C_{aliph}—Si	78.0
C_{arom}—O	107.0	As—O	64.5
Si—O	106.0	Al—C	61.6
B—N^{III}	105.0	C_{aliph}—S^{II}	61.5
B—C_{arom}	100.0	Si—S^{II}	60.9
C_{aliph}—O	93.0	C_{aliph}—As^{III}	54.6
B—C_{aliph}	89.0	N—O	37.0

Table 3. Bond energies (kcal mole^{-1}) of surrounding atoms [11].

Bond	Energy
Si—F	135
C—F	116
C_{aliph}—H	97
Si—Cl	91
C—Cl	80
Si—H	76

However, the strength of the bonds between atoms in the main chain of the macromolecule and atoms or groups attached to this chain is no less important. Table 3 shows that the fluorine–silicon and fluorine–carbon bonds possess the highest energy, which is the reason for the high thermal stability of organofluorine polymers. However, this is valid only when such bonds undergo cleavage by thermal dissociation. If the halogen can be removed in

other ways, e.g. by elimination as a hydrogen halide molecule containing a hydrogen atom from an adjacent carbon atom, the thermal stability of the polymer drops sharply. Thus poly(vinyl fluoride) and poly(vinyl chloride) show poor thermal stability owing to the ready elimination of the hydrogen halide. This applies also to poly(vinylidene chloride), poly(vinyl alcohol), and analogous compounds of general formula $[CH_2-CHX]_n$ as well as to polymers containing halogen in side-chains. Thus the higher thermal stability of pentone (the polymer of 3,3-bischloromethyloxacyclobutane) compared with poly(vinyl chloride) is due to the absence of hydrogen on the carbon atom adjacent to the chloromethyl group, which would be necessary for the formation of hydrogen chloride.

Table 4. Electronegativities of elements in different groups of Periodic System[14].

Group			
III	IV	V	VI
B—2.0	C—2.5	N—3.0	O—3.5
Al—1.5	Si—1.8	P—2.1	S—2.5
	Ge—1.8	As—2.0	Se—2.4
	Ti—1.6	V—1.9	Te—2.1
	Sn—1.7	Sb—2.1	Mo—2.1
	Sr—1.5		W—2.0
	Pb—1.6		

The energies given in Tables 2 and 3 for bonds between atoms of different elements have been calculated for homolytic dissociation of the bonds. However, all these bonds are in some measure polar, and this must always be borne in mind. Application of Pauling's concept of the electronegativity of bonds[14] is especially convenient for this purpose. The electronegativities listed in Table 4 for the most important elements can be used to determine the ionic character of bonds. If the difference in electronegativity is 1.9, such bond is 50% ionic in character; if the difference is still larger, it is more correct to regard such a compound as having an ionic structure; and if the difference is less than 1.9, the bond is covalent.

The polarity of bonds has a fundamental effect on their stability at elevated temperatures, since the more polar a bond, the more marked the decrease in its strength with rise in temperature. Organic carbon-chain compounds of high molecular weight are built up solely by covalent bonds between carbon atoms, whose electronegativity is 2.5.

From a study of polymers containing inorganic chains Andrianov[15] concluded that the stability of a bond El–El′ will be greater the less ionogenic are the bonds forming the main chain, i.e. the closer the mean electronegativity of the two elements forming the bond to that of the carbon atom. As examples of the construction of organoelementary polymers on this principle, he mentions polyorganosiloxanes and polyalumino-organosiloxanes, the chains in which are made up of alternating atoms of electropositive silicon and aluminium and of electronegative oxygen, while the mean electronegativity of bonding of these two elements approaches the electronegativity of carbon. These chains reproduce the skeleton of naturally occurring inorganic polymers—quartz, aluminosilicates—and are thermally and hydrolytically stable.

III. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF CHAIN UNIT

The thermal stability of polymers depends both on the structure of the monomeric chain unit and on that of the whole macromolecule, the presence and nature of all intermolecular bonds, and also the presence of various impurities.

Let us first examine how the structure of an individual chain unit affects thermal stability. For this purpose we regard all polymers as derivatives of two main types of macromolecular chains—polymethylene $[CH_2]_n$ and polyphenylene $[C_6H_4]_n$—as well as of various combinations thereof. These main units can also be separated by various heteroatoms or heterocycles.

Fig. 1 illustrates the results of a dynamic thermogravimetric analysis of the two extreme members—polyethylene and polyphenylene—of these classes of polymers. The thermogravimetric curves clearly show a fundamental difference in their thermal stability, which is characteristic of these two classes of substances.

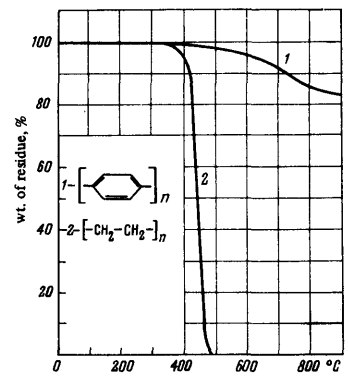
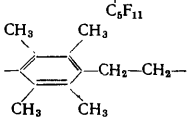
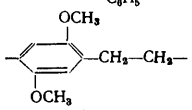
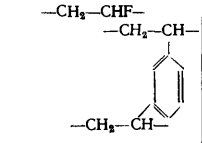


Figure 1. Dynamic thermogravimetric analysis (in vacuum, rate of heating 5 deg min^{-1}) of hydrocarbon polymers: *1*) polyphenylene; *2*) polyethylene.

The general dependence of the thermal stability of polymers on the structural unit can be illustrated by means of the relative thermal stabilities listed in Table 5. The values of the relative thermal stability of polymers (temperatures of half-decomposition T_h, at which 50% loss in weight occurs on heating for 40–45 min) are arranged in increasing order. Table 5 includes only those polymers which in a vacuum lose not less than 80–85% of their weight without the occurrence of stabilisation or cross-linking phenomena[16].

It must be remarked, however, that the half-decomposition temperature is an extremely rough indication of the thermal stability of polymers, since a far more important characteristic in this respect is the temperature of incipient decomposition of the polymer, determined as the point at which appreciable loss in weight of the heated polymer begins. The half-decomposition temperature is not characteristic of this point, but rather shows how rapidly thermal degradation of the polymer is taking place. Moreover,

Table 5. Relative thermal stability (temperature of half-decomposition) of polymers [16,17].

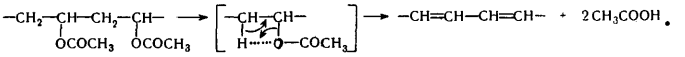
No.	Polymer	Chain unit	°C
1	Polyperfluoroheptene	$-CF_2-CF-$ C_6F_{11}	248
2	Polytetramethyl-*p*-phenylene-ethylene		265
3	Poly(methyl methacrylate) (M = 150000, obtained in the presence of benzoyl peroxide)	CH_3 $-CH_2-C-$ $COOCH_3$	283
4	Poly-α-methylstyrene	CH_3 $-CH_2-C-$ C_6H_5	287
5	Poly(propylene oxide) (atactic)	$-CH_2-CH-O-$ CH_3	295
6	Polyperfluoropropylene	$-CF_2-CF-$ CF_3	297
7	Poly(propylene oxide) (isotactic)	CH_3 $-CH_2-CH-O-$	312
8	Polyisoprene	$-CH_2-CH=C-CH_2-$ CH_3	323
9	Poly(methyl methacrylate) (M = 5100000, obtained by thermal polymerisation)	CH_3 $-CH_2-C-$ $COOCH_3$	327
10	Poly(methyl acrylate)	$-CH_2-CH-$ $COOCH_3$	328
11	Poly(ethylene oxide)	$-CH_2-CH_2-O-$	345
12	Polyisobutylene	CH_3 $-CH_2-C-$ CH_3	348
13	Polystyrene	$-CH_2-CH-$ C_6H_5	364
14	Poly-2,5-dimethoxy-*p*-phenylene-ethylene		375
15	Polychlorotrifluoroethylene	$-CF_2-CFCl-$	380
16	Polypropylene	$-CH_2-CH-$ CH_3	387
17	Poly(vinyl fluoride)	$-CH_2-CHF-$	389
18	Polydivinylbenzene		399
19	Polyethylene	$-CH_2-CH_2-$	468
20	Polybutadiene	$-CH_2-CH=CH-CH_2-$	407
21	Polytrifluoroethylene	$-CF_2-CHF-$	413
22	Polymethylene	$-CH_2-$	415
23	Polybenzyl	$-CH_2-C_6H_4-$	430
24	Poly-*p*-phenylene-ethylene	$-CH_2-C_6H_4-CH_2-$	432
25	Polytetrafluoroethylene	$-CF_2-CF_2-$	509

with aromatic and heterocyclic polymers, which are distinguished by great thermal stability, this constant is altogether unsuitable, since many polymers of this type lose less than 50% of their original weight when heated to high temperatures. Thus many polybenzimidazoles, polyquinoxalines, polyimidazopyrrolones, etc. lose only ~ 30% of their original weight at 900°C, polyphenylene only 18%, and carborane–polyamides only ~ 6%. At the present time we still have very little information on the thermal stability of polymers, so that half-decomposition temperatures, despite their inadequacy, nevertheless give some idea of the relative thermal stability of polymers.

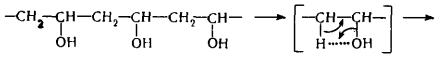
Let us examine the effect of the structure of the chain unit on thermal stability in various classes of polymers. Straight-chain polyalkenes have better thermal stability than have the branched polymers, as can be seen from a comparison of the half-decomposition temperatures of polymethylene (T_h = 415°C) and polyethylene (406°C) with those of polypropylene (387°C), polyisobutylene (348°C), and other polymers. (This question will be discussed in greater detail in Section IV, 3.)

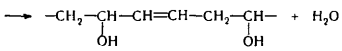
The presence of a double bond in the chain hardly diminishes the thermal stability at all, as can be seen from a comparison of polyethylene with polybutadiene (T_h = 407°C). The thermal stability of *cis*- and *trans*-isomers shows no fundamental difference, as evidenced by natural rubber and gutta-percha, and also by synthetic polyisoprene[18].

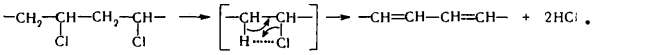
Several polymers are characterised by low thermal stability owing to the presence in their chain units of such groups and atoms as OH, Cl, RCO, etc., which are readily eliminated as water, hydrogen chloride, alcohol, ammonia, etc. Examples of such compounds are poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride), etc. The breakdown of poly(vinyl acetate) yields polyvinylene via an intermediate activated complex:



Poly(vinyl alcohol) and poly(vinyl chloride) also decompose:







The formation of double bonds sharply diminishes the stability of adjacent hydroxy-groups, since the latter are in the β-position with respect to the double bond, and are especially easily split off. Therefore poly(vinyl chloride), poly(vinyl alcohol), and various derivatives easily eliminate almost 100% of halogen or hydroxyls, as the hydrogen halide or water, at relatively low temperatures[19,20]. Fig. 2 shows the loss in weight of poly(vinyl alcohol) and polyethoxyethylene compared with polyethylene, and Fig. 3 that of poly(vinyl chloride) and poly(vinylidene chloride), as a result of being heated at various temperatures.

In most cases replacement of hydrogen by fluorine atoms enhances the thermal stability of polymers, this being due to the higher energy of the carbon–fluorine bond compared with the carbon–hydrogen bond (see Table 3). Fig. 4 shows the quantity of volatile products lost by various fluorinated polymers when heated at various temperatures for 2 h.[21,22] The most stable proved to be polytetrafluoroethylene (T_h = 509°C). The other copolymers and polymers in Fig. 4 show lower thermal stability. Partial replacement of hydrogen by fluorine atoms, as e.g. in poly(vinylidene fluoride), or the presence of chlorine atoms in polychlorotrifluoroethylene lowers the thermal stability. Copolymers of trifluoronitrosomethane have the lowest thermal stability, since they contain –N–O– bonds, which are less stable than –C–C– bonds (Tables 1 and 2). On the other hand, –C–O– bonds are stable, and poly(hexafluoropentamethylene adipate) therefore possesses higher thermal stability. Polymers of fluorinated ethylenes and polyethylene are

arranged in the following sequence of diminishing thermal stability (T_h)

$$(-CF_2-CF_2-)_x > (-CH_2-CF_2-)_x > (-CF_2-CHF-)_x > (-CH_2-CH_2-)_x >$$
(T_h=509°) (T_h=445°) (T_h=412°) (T_h=406°)
$$> (-CH_2-CHF-)_x$$
(T_h=388°)

Only poly(vinyl fluoride) is inferior to polyethylene, while the other fluorinated polymers surpass it in thermal stability[22].

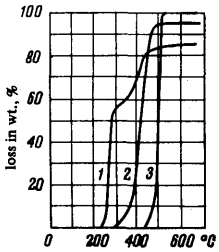


Figure 2. Dynamic thermogravimetric analysis (rate of heating 2 deg min^{-1}) of vinyl polymers[19]:
1) poly(vinyl alcohol); *2*) poly(ethyl vinyl ether); *3*) polyethylene.

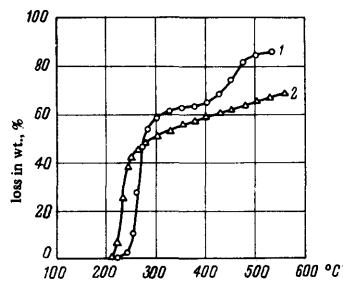


Figure 3. Isothermal thermogravimetric analysis (in atmosphere of nitrogen)[20] of:
1) poly(vinyl chloride); *2*) poly(vinylidene chloride).

A factor of fundamental importance in the relation between thermal stability and structure is the ability of a polymer to decompose on heating with formation of a volatile monomer. All polymers can be divided into two groups according to their behaviour on pyrolysis: polymers in the first group form monomers and other volatile products on thermal decomposition, and either volatilise completely or leave a small non-volatile residue when heated; polymers of the second group do not form volatile monomers, but are converted mainly into non-volatile products. The former group includes vinyl and diene polymers; the second group contains mainly polymers with benzene rings or heterocycles in the main chain.

The presence of benzene rings in the chain enhances the thermal stability of a polymer in comparison with polyethylene (T_h = 406°C), as is evident from the examples of polybenzyl (430°C) and poly-*p*-xylylene (432°C). The effect of position isomerism of the substituents in the aromatic ring must be noted here, as can be seen from Fig. 5, which gives thermogravimetric curves for polymeric *m*- and *p*-xylylenes and their copolymers.

Polymers containing aromatic rings linked together either directly or through various radicals are distinguished by great thermal stability. Table 6 gives values of the relative thermal stability of several polymers containing aromatic rings, determined at the temperature at which the weight of a specimen is halved in 2 h.[17]

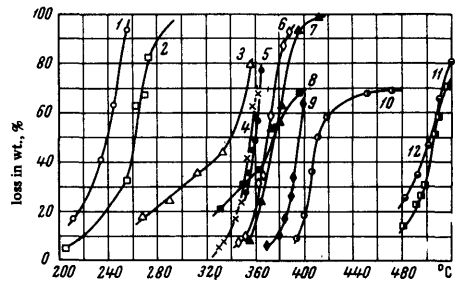


Figure 4. Isothermal thermogravimetric analysis (each point corresponds to a separate specimen heated in a vacuum for 2 h) of various fluorine-containing polymers[22]:
1) copolymer of trifluoronitrosomethane with trifluoroethylene;
2) copolymer of trifluoronitrosomethane with tetrafluoroethylene;
3) poly(hexafluoropentamethylene adipate);
4) polychlorotrifluoroethylene;
5) copolymer of vinylidene fluoride (36%) with chlorotrifluoroethylene (64%);
6) copolymer of vinylidene fluoride (55%) with chlorotrifluoroethylene (45%);
7) copolymer of vinylidene fluoride (77%) with chlorotrifluoroethylene (23%);
8) copolymer of octafluorocyclohexa-1,3-diene with butadiene;
9) copolymer of vinylidene fluoride with hexafluoropropylene;
10) poly(vinylidene fluoride);
11) copolymer of tetrafluoroethylene with hexafluoropropylene;
12) polytetrafluoroethylene.

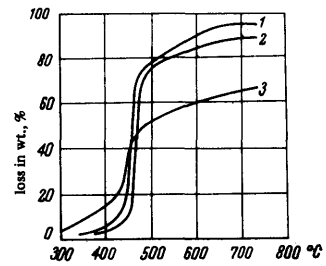
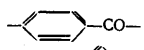
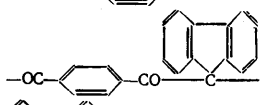
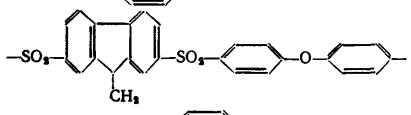
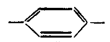
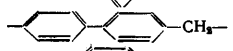
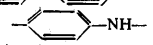
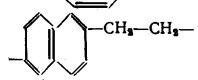
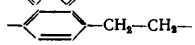
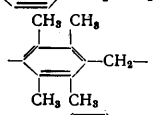
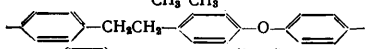
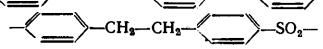
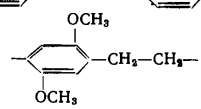
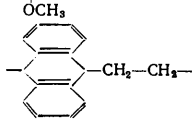
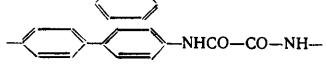
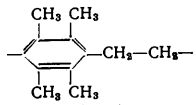
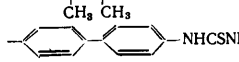
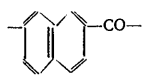


Figure 5. Thermal stability, determined by dynamic thermogravimetric analysis (rate of heating 2.5 deg min^{-1})[22], of polyphenylene-ethylenes:
1) *meta*-isomer; *2*) copolymer of *meta*- and *para*-isomers (1 : 1);
3) *para*-isomer.

The polymers listed in Table 6 can be divided into two types according to their behaviour on heating. The first type includes polymers whose chain unit is made up of such groups as *p*-phenylene (No. 4), *m*-phenylene (5), *pp'*-biphenylylenemethylene (6), tetramethyl-*p*-phenylenemethylene (10), tetramethyl-*p*-phenylene-ethylene (16), *p*-phenyleneimine (7), *pp'*-biphenylylenedi-imineoxalyl (15), naphthylenecarbonyl (18), *p*-phenylenecarbonyl (1), terephthaloylfluorenylidene (2), and also the condensation product of fluorene-2,7-disulphonyl chloride and diphenyl ether (3).

Table 6. Relative thermal stability of polymers (temperature at which the weight of the polymer is halved in 2 h).

No.	Chain unit	Stability, °C	Softening point, °C
1		700	>400
2		640	>400
3		>690	>400
4		<680	>400
5		540	400
6		525	>400
7		485	>400
8		450	>400
9		430	>400
10		430	225—230
11		425	150
12		415	225—230
13		375	215
14		360	>400
15		350	400
16		265	480
17		230	does not soften, but volatilises completely at 350°C
18		<250	>400

The second type includes 2,5-dimethyoxy-1,4-phenylene-ethylene (13), *p*-phenylene-ethylene (9), naphthylene-ethylene (8), anthrylene-ethylene (14), *pp'*-biphenylylenethioureylene (17), *pp'*-biphenylylene-ethylenephenoxy (11), and *p*-phenylene-ethylene-*p*-phenylenesulphonyl (12).

Compounds of the first type are characterised by a rapid loss of part of their weight during the initial stage of heating, after which the residue either undergoes no further change or decomposes slowly.

Polymers of the second type lose weight more slowly on being heated, but these losses are larger than in the first type. They all contain the ethylene group, which is probably readily eliminated. Polymers containing a carbonyl group as linking unit show the greatest thermal stability. An exception is the thermally least stable naphthylenecarbonyl, which already shows appreciable loss in weight at around 250°C, but on further heating to 500°C decomposes only slightly: this is, perhaps, due to contamination with products of low molecular weight.

Fig. 6 shows the loss in weight of a series of polyalkylenephenylenes when heated in a vacuum for 2 h.[24] It includes for comparison the curve for polytetrafluoroethylene.

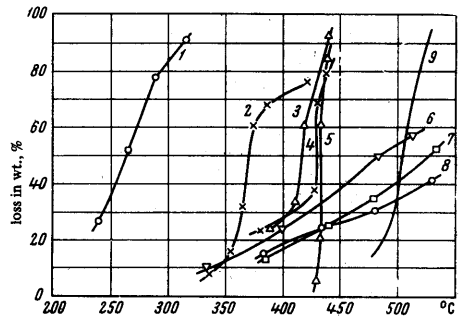


Figure 6. Isothermal thermogravimetric analysis (heating in a vacuum for 2 h) of various polyalkylenephenylenes[24]:
1) polytetramethyl-*p*-phenylene-ethylene; *2*) poly-2,5-dimethoxy-*p*-phenylene-ethylene; *3*) poly-2,5-dimethyl-*p*-phenylenemethylene; *4*) polytetramethyl-*p*-phenylenemethylene; *5*) poly-*p*-phenylene-ethylene; *6*) poly-*pp'*-biphenylylenemethylene; *7*) poly-*m*-phenylene; *8*) poly-*p*-phenylene; *9*) polytetrafluoroethylene.

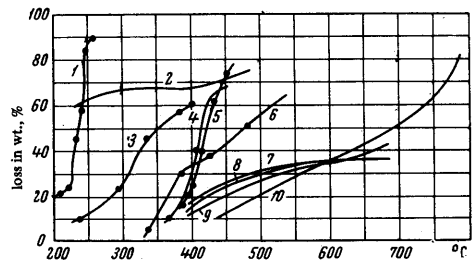
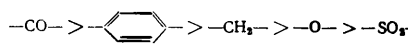


Figure 7. Thermal stability of aryl polymers containing various bridging groups, determined by isothermal thermogravimetric analysis[17] (heating in a vacuum for 2 h):
1) poly-*pp'*-biphenylylenethioureylene; *2*) polynaphthylenecarbonyl; *3*) poly-*pp'*-biphenylylenedi-imineoxalyl; *4*) poly-*p*-phenylene-ethylene-*p'*-phenylenesulphonyl; *5*) poly-*pp'*-biphenylylene-ethylenephenoxy; *6*) *p*-phenyleneimine; *7*) polymer of fluorene-2,7-disulphonyl chloride and diphenyl ether; *8*) polymer of terephthaloyl chloride and naphthalene; *9*) polyphenylenecarbonyl; *10*) polymer of terephthaloyl chloride and fluorene[17].

The nature of the bridging groups joining arylene units in polymers also has a substantial influence on thermal stability, as can be seen from Fig. 7, which gives curves showing the loss in weight of several polymers when heated at various temperatures for 2 h.[17] It can be concluded from these results that the thermal stability of polymers

containing aromatic rings in the chain diminishes according to the nature of the bridging groups in the sequence



The presence of hydroxyl and other substituents in the aromatic ring affects all the properties of the polymer, including its thermal stability. Thus phenol–formaldehyde polymers, which are fairly thermostable substances[25], clearly confirm this principle: the introduction of substituents into the benzene ring results in diminished thermal stability. The thermogravimetric curves for poly-*p*-phenylene and resite, reproduced in Fig. 8, show that the thermal stability of the latter is considerably lower than that of the former, which is explained by the presence of methylene and hydroxyl groups in the benzene rings of resite.

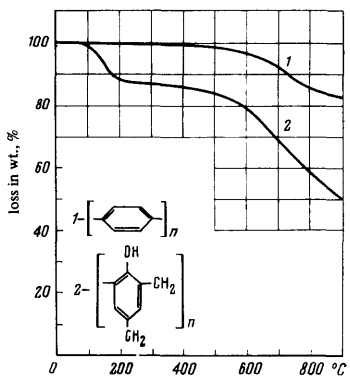


Figure 8. Dynamic thermogravimetric analysis (heating in argon at 15 deg min^{-1}) of:
1) poly-*p*-phenylene; *2*) resite.

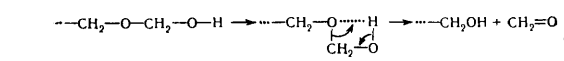
Table 7. Amine–formaldehyde polymers[27].

Amine	Loss in wt., %, at 330°C	Loss in wt., %, at 900°C	Temp. of max. gas evolution, °C
Fuchsine	19	35	700
p-Aminophenol	15	47	600
Melamine	36	56	450, 500
Dicyanodiamide	37	62	200, 700
2,6-Diaminopyridine	30	56	600
m-Phenylenediamine	20	57	600
Urea	36	70	300
Aniline	47	81	650

Phenoplasts can operate at 175°C for an indefinite period, but at 200°C for only a few hours; above 200°C their stability drops sharply. As a comparison it may be mentioned that the temperature at which thermal degradation of phenol–formaldehyde polymers begins in an atmosphere of hydrogen is 432°C, as determined by thermoparticulate analysis, whereas the corresponding temperatures for poly(methyl methacrylate) and polystyrene are 310° and 337°C respectively[26].

Many products of the polycondensation of formaldehyde with aromatic amines, which have been prepared by Sergeev et al.[27], are characterised by great thermal stability. When heated to 330°C they lose 15–30% of their weight, but when heated to 900°C they form a non-volatile residue constituting up to 65% of the weight of the original polymer (Table 7). The most thermostable are products of the polycondensation of formaldehyde with *p*-aminophenol.

The introduction of ethereal oxygen into the main chain of a polymer lowers its thermal stability. Thus the thermal stability T_h of polyformaldehyde, poly(ethylene oxide), and isotactic and atactic poly(propylene oxide) (170°, 345°, 312°, and 295°C respectively) is lower than for the corresponding hydrocarbon polymers—polymethylene, polyethylene, and polypropylene (415°, 406°, and 387°C).[16,21] Owing to the polarity of the C–O bond, polyethers show a great tendency to thermal degradation with liberation of the monomer or its conversion products:



As in the case of polyalkenes the presence of lateral substituents lowers the thermal stability. It is interesting that atactic poly(propylene oxide) is thermally less stable than the isotactic isomer. The irregular arrangement of substituents is obviously the cause of structural inhomogeneities facilitating breakdown of the polymer chain.

Aromatic polyethers, in contrast to the aliphatic polymers, are extremely thermostable[28]. Fig. 9 shows thermograms for poly-(2,6-dimethyl-1,4-phenylene oxide) in an atmosphere of nitrogen[29]. It is seen that the poly(phenylene oxide) begins to decompose at 430°C.

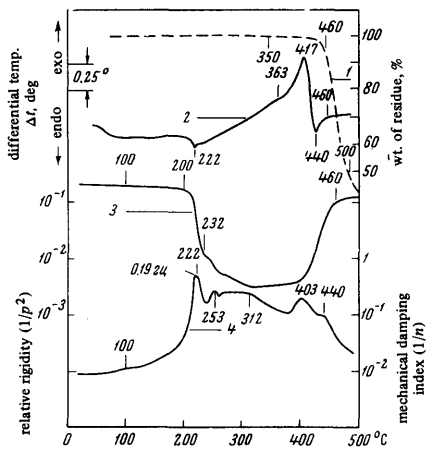


Figure 9. Thermograms of poly-(2,6-dimethyl-*p*-phenylene oxide) determined in an atmosphere of nitrogen[22]:
1) dynamic thermogravimetric analysis (rate of heating 5 deg min^{-1}); *2*) differential thermal analysis (5 deg min^{-1}); *3*) thermomechanical torsion method (2 deg min^{-1}); *4*) thermomechanical torsion method (2 deg min^{-1}).

The thermal stability of polyesters depends on their structure. Table 8 gives Ritchie's measurements[30] of the temperatures at which a series of unsaturated polyesters and their copolymers begin to decompose. It is seen from Table 8 that the temperature at which carbon dioxide is eliminated lies in the range 280–345°C depending on the structure of the polyester. Formation of unsaturated products and aldehydes takes place over practically the same

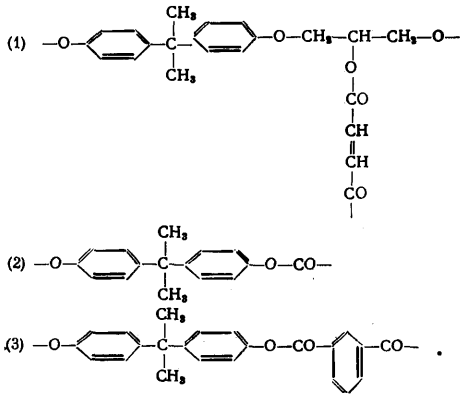
temperature range. It must be noted that a polyester of the saturated succinic acid begins to break down at a higher temperature than is found for polyesters of the unsaturated fumaric acid.

Table 8. Temperatures of start of thermal decomposition of various unsaturated polyesters* and their copolymers[30].

Polyester	Initial temperature, °C			
	evolution of CO_2	formation of unsaturateds	formation of aldehydes	formation of methyl methacrylate
Poly(ethylene fumarate)	295	305	305	—
Poly(neopentyl fumarate)	290	335	290	—
Poly-(*p*-phenylene fumarate)	280	+	+	—
Poly(ethylene succinate)	345	320	330	—
Ethylene fumarate + methacrylate copolymer	305	305	310	265
Neopentyl fumarate + methyl methacrylate copolymer	310	380	310	260
Methyl fumarate + methacrylate copolymer	—	—	—	250
Poly(methyl methacrylate)	—	—	—	240

* Up to 500°C neither ethylene, acetylene, nor aldehyde evolved.

It is seen from the above data that aliphatic polyesters and their copolymers have no great thermal stability. In contrast to them, polyesters of arenediols and aromatic dicarboxylic acids—"polyarylates"—are highly thermostable substances. The curves in Fig. 10 show the relative rates of decomposition of poly-(2,2-di-*p*-phenylenepropane isophthalate) (a polyarylate), a polycarbonate, and an epoxide resin at 400°C. It is seen that the polyarylate considerably surpasses the polycarbonate and the epoxide resin in thermal stability. These three polymers resemble one another in the structure of the principal chain unit, in which a 2,2-diphenylpropane-*pp'*-diol residue is present:



The differences in their thermal stability depend on the structure of the second component of the chain unit. Therefore the thermal stability of polyarylates should be improved by removing the aliphatic part of the chain unit, as also on replacing isophthalic by terephthalic acid. Fig. 11 illustrates the thermal stability of polyarylates of phenolphthalein with isophthalic and terephthalic acids: the extent of decomposition of the former considerably exceeds that of the latter at the same temperatures[32].

The thermal stability of polyarylates is greatly influenced by the nature of substituents in the central dihydric phenol. Polyarylates based on diphenylfluorene-*pp'*-diol are distinguished by especially high thermal stability, as can be seen from Fig. 12. These polyarylates have also a higher photostability[33].

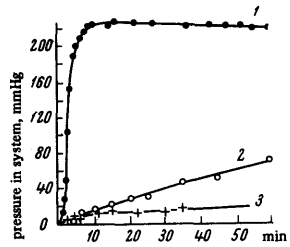


Figure 10. Rate of thermal degradation at 400°C of some polymers based on 2,2-diphenylpropane-*pp'*-diol (dian), determined from pressure of gases evolved[31]:
1) epoxide polymer obtained by hardening the epoxide oligomer ED-6 with maleic anhydride; *2*) poly(dian carbonate); *3*) poly(dian isophthalate) (polyarylate D-2).

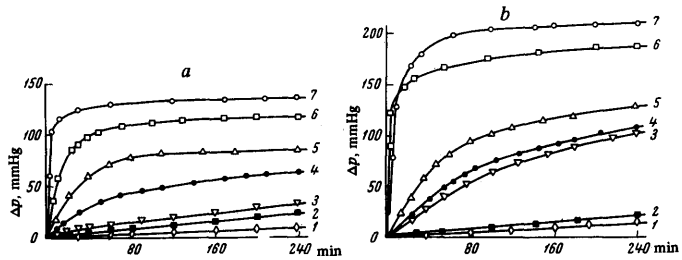
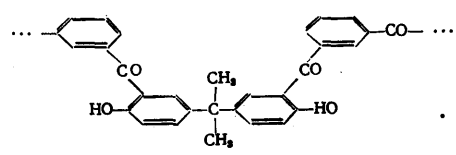


Figure 11. Kinetics of the degradation, determined from the increase in pressure in a closed system[32], of the polyarylates of phenolphthalein and: *a*) terephthalic acid; *b*) isophthalic acid. Temperature (°C): *1*) 350; *2*) 375; *3*) 400; *4*) 425; *5*) 450; *6*) 475; *7*) 500.

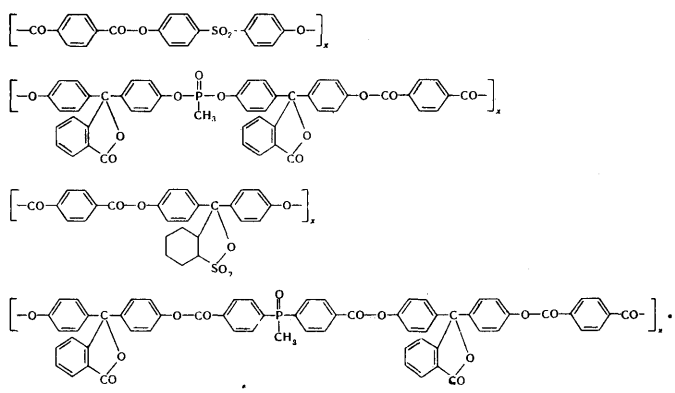
It has been shown with the polyarylates that the incorporation of certain groups may produce "self-protective polymers", which contain various groups and atoms enhancing their stability and protecting them from thermal and chemical breakdown. Self-protective polyarylates have been obtained in several ways[34,37]. Thus the Fries rearrangement or the use of trihydric phenols yields polyarylates containing free phenolic hydroxyls



Such polyarylates have improved thermal stability, and are also more resistant to the action of light and to hydrolysis[34,35].

An equally favourable effect is produced by introducing sulphonyl groups[36] or residues of phosphinic acids[37] into

the polyarylate molecule, as has been shown for the compounds



The introduction of residues of *p*-iodobenzoic acid as end-groups has also proved extremely effective[38]. Such self-protective polyarylates are considerably more resistant to the action of high temperatures.

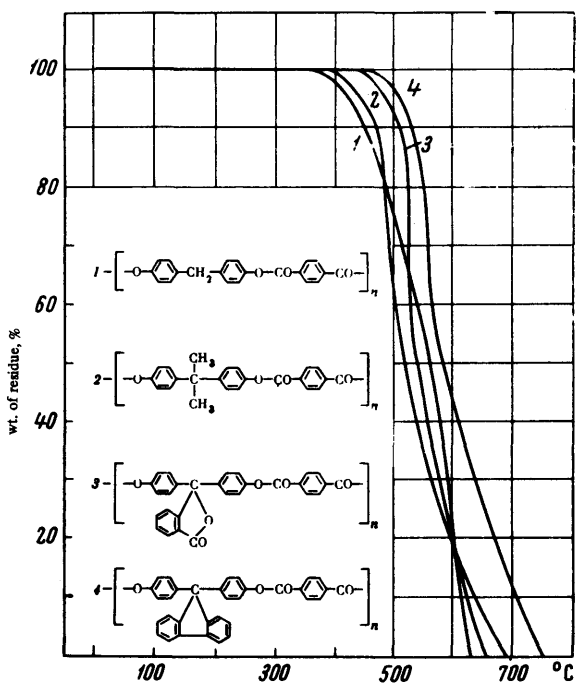


Figure 12. Dynamic thermogravimetric analysis (heating in nitrogen at 4 deg min^{-1})[40] of the polyterephthalates of:
1) diphenylmethane-*pp'*-diol; *2*) 2,2-diphenylpropane-*pp'*-diol; *3*) phenolphthalein; *4*) 9,9-diphenylfluorene-*pp'*-diol.

There are also several extremely thermostable compounds among heterochain polyamides. Aliphatic polyamides have a lower thermal stability than have aromatic polyamides. Thus polyhexano-amide fibre begins to decompose at 400°C, the maximum rate of decomposition occurring over the range 400–436°C.[29,39] Fig. 13 gives thermograms for polyhexano-amide characterising its thermal stability. In general the breakdown of polyamides begins with cleavage of the amide bond. Therefore they start to decompose at temperatures of around 350°C, independently of the structure of the rest of the chain unit, as can be seen from Fig. 14. Nevertheless, aromatic polyamides are more thermostable.

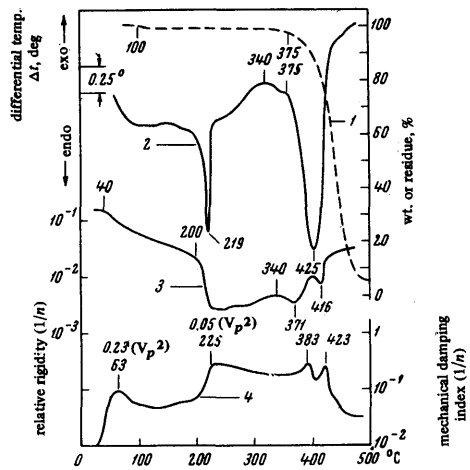


Figure 13. Thermograms of polyhexanoamide[29]:
1) dynamic thermogravimetric analysis (heated in nitrogen at 5 deg min^{-1}); *2*) differential thermal analysis; *3*) thermomechanical torsion method (rate of heating 2 deg min^{-1}); *4*) thermomechanical torsion method.

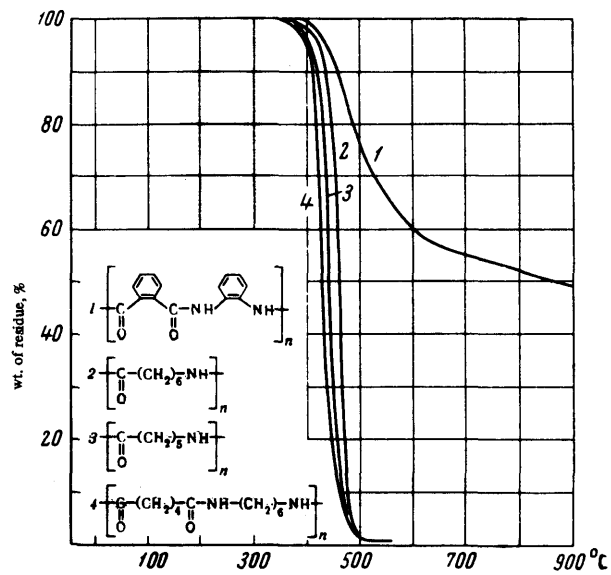
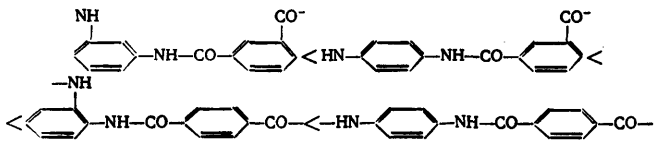


Figure 14. Dynamic thermogravimetric analysis (heated in helium at 5 deg min^{-1}) of polyamides:
1) poly-*m*-phenyleneisophthalamide; *2*) poly-ω-heptanoamide; *3*) polyhexanoamide; *4*) polyhexamethyleneadipamide.

Aromatic polyamides obtained from phenylenediamines and benzenedicarboxylic acids can be arranged according to increasing thermal stability, in the sequence



i.e. polyamides of isophthalic acid are inferior to those of terephthalic acid, just as polyamides from *p*-phenylenediamine are more stable than those from *m*-phenylenediamine (Fig. 15).[41] Thermogravimetric analysis of the polyamide obtained from anilinephthalein and terephthalic acid has shown that this polymer possesses high thermal stability (Fig. 16).[42]

Ordinary polyurethanes begin to decompose at a temperature above 220°C. The thermal stability of polyurethanes can be increased by replacing the hydrogen atoms of the carbamate group by an alkyl or an acyl group[43], and also by using di-isocyanates, in which the isocyanate groups are separated from an aromatic ring by methylene groups, which hinders intramolecular resonance[44-46].

As we have already seen, replacing aliphatic by aromatic groups in the chain unit produces a sharp increase in the thermal stability of polymers. The same result is achieved also by introducing heterocyclic groups of aromatic character into the chain unit, which yields such polymers as polybenzimidazoles, polybenzoxazoles, polyimides, polybenzothiazoles, pyrrones, polypyrazoles, polythiazoles, polyoxadiazoles, polytriazoles, etc. A large number of polymers of this type have now been prepared, and their properties investigated. The results have been summarised in reviews[3,4,8,48,49].

An important feature of these polymers—"polyheteroarylenes"—is their extremely high thermal stability (Table 9). The results of a thermogravimetric analysis of four polybenzimidazoles are plotted in Fig. 17. Polymers containing an aliphatic residue in the chain unit begin to decompose above 450°C, and those containing phenylene groups above 550°C. Even at 900°C the losses in weight of the last two polymers are only 30%.

Table 9. Thermal stability (temperature at which decomposition begins) of some polymers containing heterocycles in the chain.

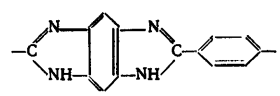
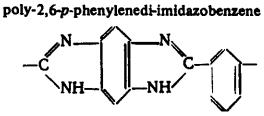
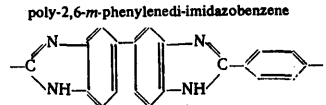
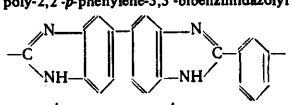
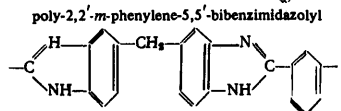
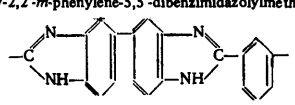
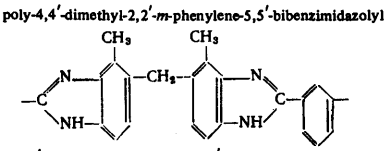
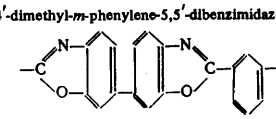
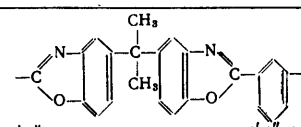
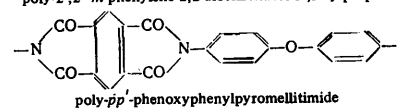
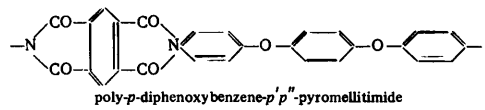
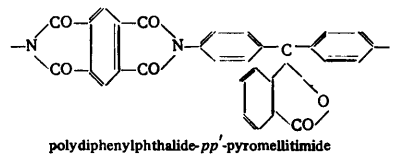
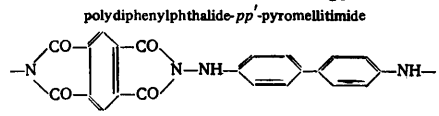
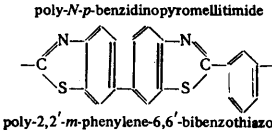
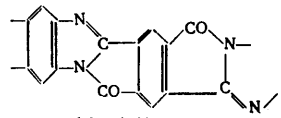
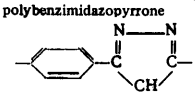
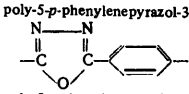
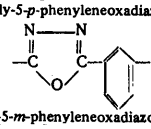
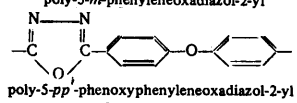
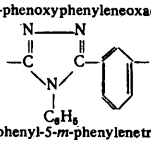
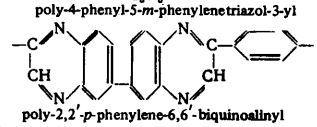
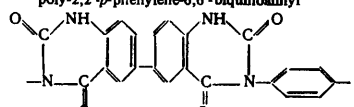
Starting materials		Chain unit and polymer	°C	Ref.
dicarboxylic acid or derivative	second component			
Diphenyl terephthalate	benzene-1,2,4,5-tetra-amine	 poly-2,6-*p*-phenylenedi-imidazobenzene	500	50
Diphenyl isophthalate	benzene-1,2,4,5-tetra-amine	 poly-2,6-*m*-phenylenedi-imidazobenzene	500	50
Diphenyl terephthalate	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*p*-phenylene-5,5′-bibenzimidazolyl	550	50
Diphenyl isophthalate	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*m*-phenylene-5,5′-bibenzimidazolyl	550	50
Diphenyl	diphenylmethane-3,3′,4,4′-tetra-amine	 poly-2,2′-*m*-phenylene-5,5′-dibenzimidazolylmethane	490	51
Diphenyl isophthalate	2,2′-dimethylbiphenyl-3,3′,4,4′-tetra-amine	 poly-4,4′-dimethyl-2,2′-*m*-phenylene-5,5′-bibenzimidazolyl	490	52
Diphenyl isophthalate	2,2′-dimethyldiphenyl-methane-3,3′,4,4′-tetra-amine	 poly-4,4′-dimethyl-*m*-phenylene-5,5′-dibenzimidazolylmethane	400	52
Diphenyl isophthalate	4,4′-diaminobiphenyl-3,3′-diol	 poly-2,2′-*m*-phenylene-6,6′-bibenzoxazolyl	500	53

Table 9. (cont'd).

Starting materials: dicarboxylic acid or derivative	Starting materials: second component	Chain unit and polymer	°C	Ref.
Diphenyl isophthalate	3′,3″-diamino-2,2-diphenylpropane-4′,4″-diol	 poly-2′,2″-*m*-phenylene-2,2-dibenzoxazol-5′,5″-ylpropane	500	54
Pyromellitic anhydride	phenoxybenzene-*pp*′-diamine	 poly-*pp*′-phenoxyphenylpyromellitimide	450	55
Pyromellitic anhydride	*p*-diphenoxybenzene-*p*′*p*″-diamine	 poly-*p*-diphenoxybenzene-*p*′*p*″-pyromellitimide	—	56
Pyromellitic anhydride	anilinephthalein	 polydiphenylphthalide-*pp*′-pyromellitimide	450	57
Pyromellitic anhydride	biphenylylene-*pp*′-di hydrazine	 poly-*N*-*p*-benzidinopyromellitimide	400	58
Diphenyl isophthalate	4,4′-diaminobiphenyl-3,3′-dithiol	 poly-2,2′-*m*-phenylene-6,6′-bibenzothiazolyl	550	59—61
Pyromellitic anhydride	benzene-1,2,4,5-tetra-amine	 polybenzimidazopyrrone	450	62
p-Bisdiazoxylene	*p*-diethynylbenzene	 poly-5-*p*-phenylenepyrazol-3-yl	550	63
Terephthaloyl chloride	terephthalodihydrazide	 poly-5-*p*-phenyleneoxadiazol-2-yl	400	64
Isophthaloyl chloride	isophthalodihydrazide	 poly-5-*m*-phenyleneoxadiazol-2-yl	400	64
Phenoxybenzene-*pp*′-dicarbonyl chloride	phenoxybenzene-*pp*′-dicarbohydrazide	 poly-5-*pp*′-phenoxyphenyleneoxadiazol-2-yl	430	65
Polyisophthalohydrazide	aniline	 poly-4-phenyl-5-*m*-phenylenetriazol-3-yl	450	66
p-Diglyoxyloylbenzene	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*p*-phenylene-6,6′-biquinoallinyl	470	67
Benzidine-3,3′-dicarboxylic acid	*p*-phenylene di-isocyanate	 poly-1,1′,2,2′,3,3′,4,4′-octahydro-2,2′,4,4′-tetraoxo-3,3′-*p*-phenylene-6,6′-biquinazolinyl	540	68

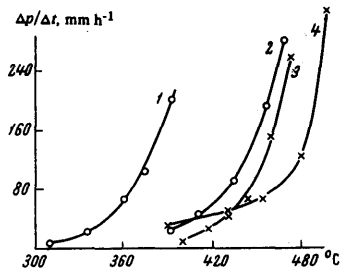


Figure 15. Temperature variation in rate of decomposition, determined from pressure of gases evolved[41], of aromatic polyamides: *1*) poly-*m*-phenyleneisophthalamide; *2*) poly-*m*-phenyleneterephthalamide; *3*) poly-*p*-phenyleneisophthalamide; *4*) poly-*p*-phenyleneterephthalamide.

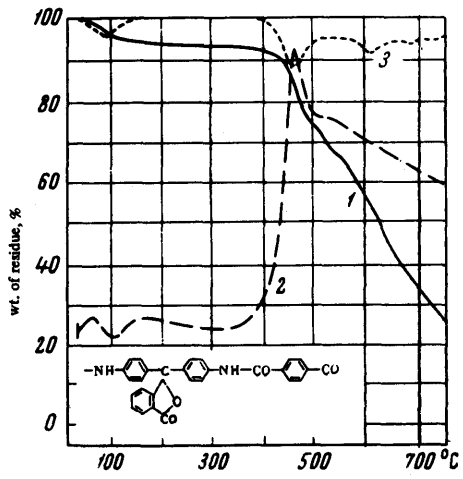


Figure 16. Thermal analysis (heated in nitrogen at 3.7 deg min^{-1})[47] of polyamide obtained from anilinephthalein and terephthalic acid: *1*) dynamic thermogravimetric analysis; *2*) differential thermal analysis; *3*) differential thermogravimetric analysis.

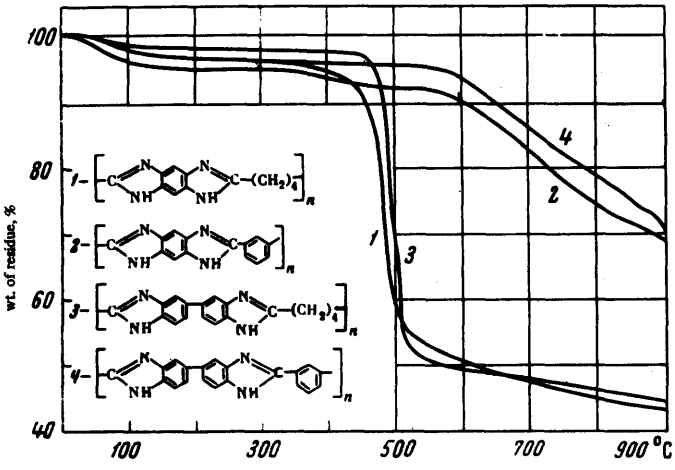


Figure 17. Dynamic thermogravimetric analysis of polybenzimidazoles[50] (heated in nitrogen at 2.5 deg min^{-1}).

The products obtained by the polycondensation of tetraamines with anhydrides of tetracarboxylic acids are more thermostable. Fig. 18 illustrates the results of a thermogravimetric analysis of two polybenzimidazoimides (pyrrones) prepared from pyromellitic anhydride; they have a ladder structure and are distinguished by great thermal stability.

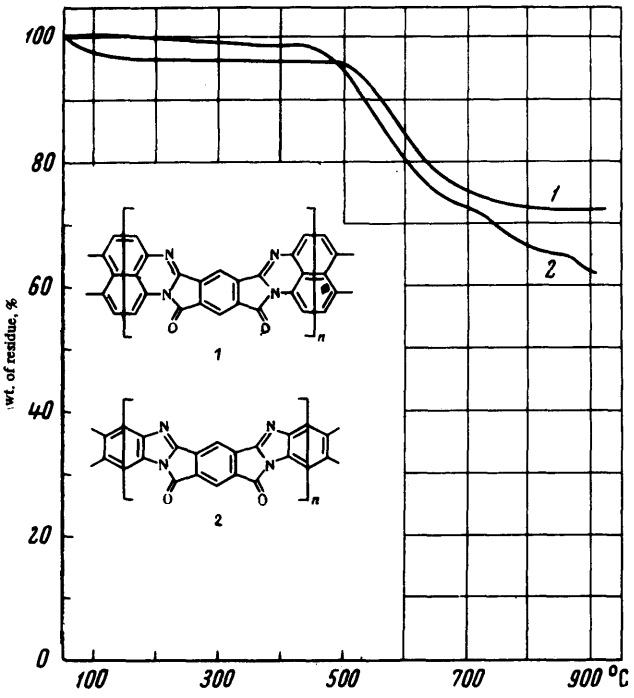


Figure 18. Dynamic thermogravimetric analysis of polybenzimidazoimides[62] (heated in nitrogen at 6 deg min^{-1}).

Polyimides also constitute an extremely thermostable class of polymers. Thus thermogravimetric analysis of four polypyromellitimides shows (Fig. 19) that a polymer containing a biphenylylene group is the most thermostable, polymers containing a *m*-phenylene or a diphenylene oxide group are not quite so good, and the most unstable is the polymer containing a diphenylenemethane group. Soluble polypyromellitimides obtained from anilinephthalein and diaminodiphenylfluorene are extremely thermostable (Fig. 20). Results of a dynamic thermogravimetric analysis of a polyimide and of several vinyl polymers are illustrated in Fig. 21.

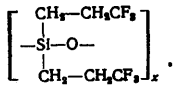
Fig. 22 gives for comparison results of a thermogravimetric analysis of polyquinoxaline, polybenzoxazole, and polyoxadiazole. Curves for polyquinazolinediones—representatives of a new class of thermostable polymers—are given in Fig. 23.

In a large group of thermostable polymers other elements accompany carbon in the chain of the macromolecule. The most interesting are polymers containing silicon, boron, phosphorus, and various metals. The chief factor determining the thermal stability of these polymers is the energy of the bond between atoms in the main chain

and those surrounding it. A characteristic feature of polydiphenylsilanes is their tendency to oxidise when heated in the air to 300°C. As a consequence, the weight of a specimen increases, as shown in Fig. 24.

Fig. 25 gives thermogravimetric curves for a series of organosilicon polymers. The thermal stability of polysiloxanes containing aromatic radicals is higher than that of those containing aliphatic radicals. The introduction of phenylene groups into the main chain produces an especially marked increase in thermal stability, as occurs with silaphenylene polymers.

Polyfluoroalkylsiloxanes are also characterised by enhanced thermal stability, but both this and their hydrolytic stability depend on the position of the fluorine relative to the silicon, as is evident from Table 10.[71] The most thermostable were polyfluoroalkylsiloxanes containing fluorine atoms in the γ-position relative to the C–Si bond, and having the structure



A large number of organoboron polymers are known, containing B–C, B–N, and other bonds[73]. However, very few data are at present available on their thermal stability. Thermogravimetric analysis of a polybenzoborimidazoline and of a polybenzimidazole containing phosphorus shows

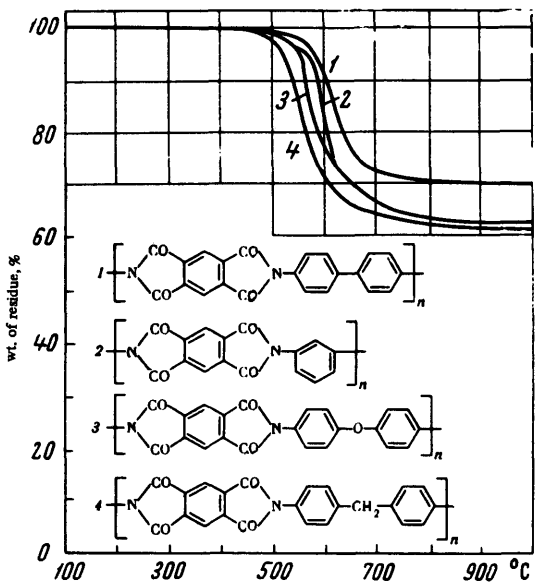


Figure 19. Dynamic thermogravimetric analysis of polypyromellitimides[70] (heated in dry helium at 3 deg min^{-1}).

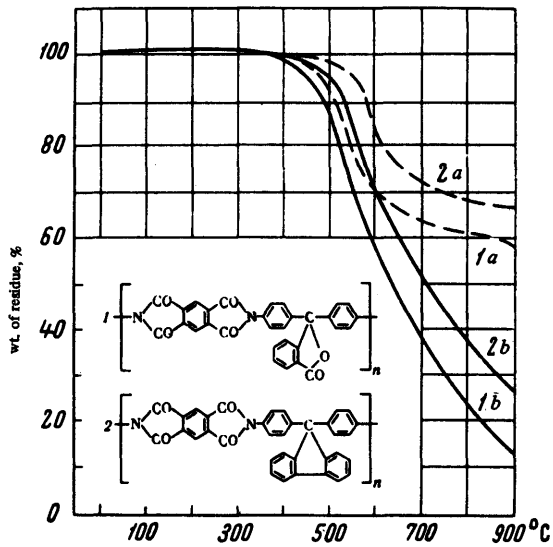


Figure 20. Dynamic thermogravimetric analysis of polypyromellitimides prepared from:
1) anilinephthalein; *2*) 9,9-diphenylfluorene-*pp'*-diamine[57]. Heated at 5 deg min^{-1}: *a*) helium; *b*) air.

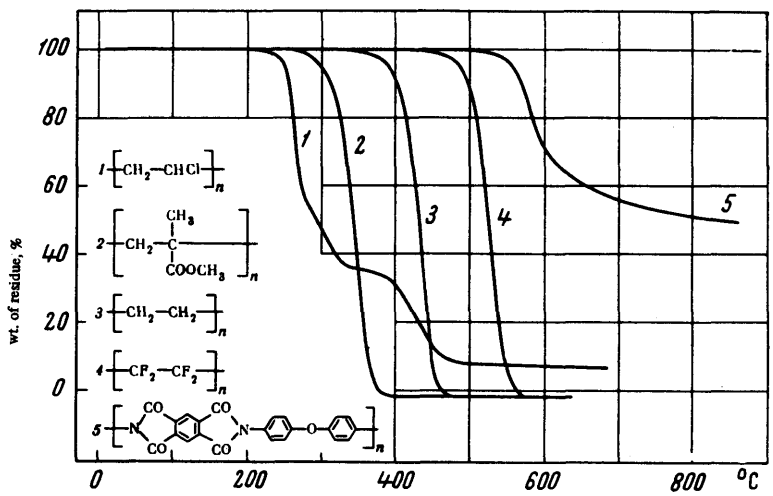


Figure 21. Dynamic thermogravimetric analysis of polymers in nitrogen (rate of heating 5 deg min^{-1})[69].

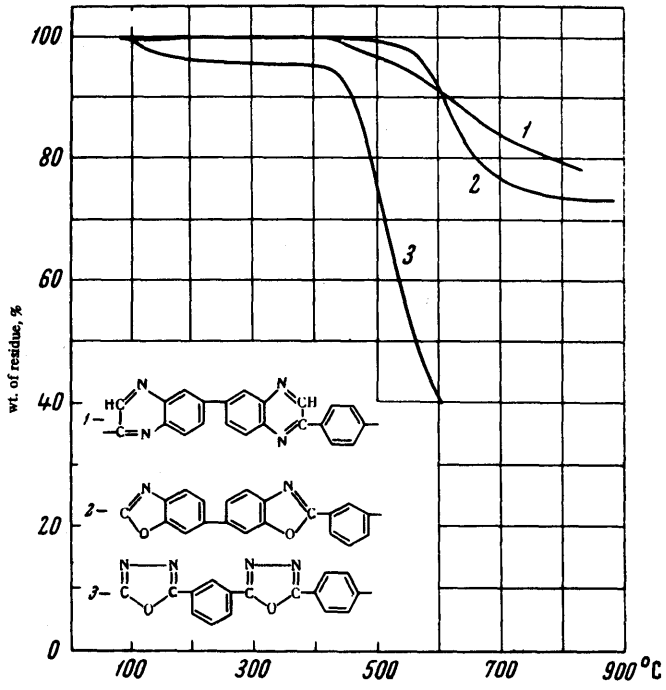


Figure 22. Dynamic thermogravimetric analysis (in nitrogen) of the polymers:
1) poly-2,2′-*p*-phenylene-6,6′-biquinoxalinyl; *2*) poly-2,2′-*m*-phenylene-6,6′-bibenzoxazolyl; *3*) poly-5-*m*-phenyleneoxadiazol-2-yl-5′-*p*-phenyleneoxadiazol-2′-yl.

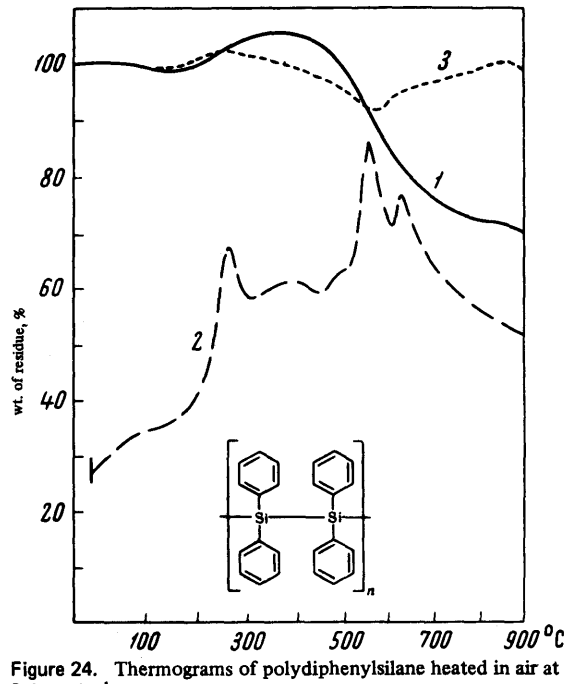


Figure 24. Thermograms of polydiphenylsilane heated in air at 9 deg min^{-1}:
1) dynamic thermogravimetric analysis; *2*) differential thermal analysis; *3*) differential thermogravimetric analysis.

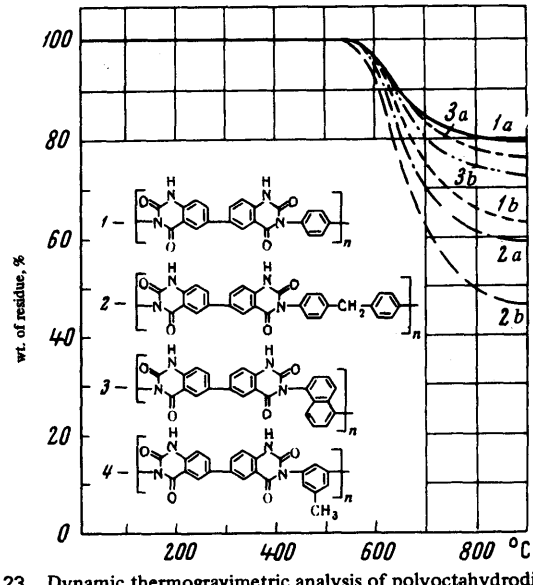


Figure 23. Dynamic thermogravimetric analysis of polyoctahydrodioxobiquinazolinyls[68] heated at 6 deg min^{-1} in:
a) nitrogen; *b*) air.

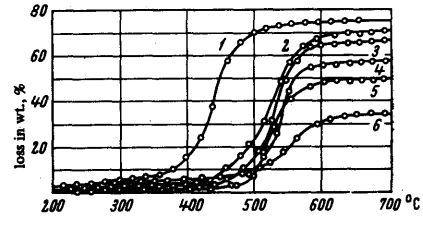
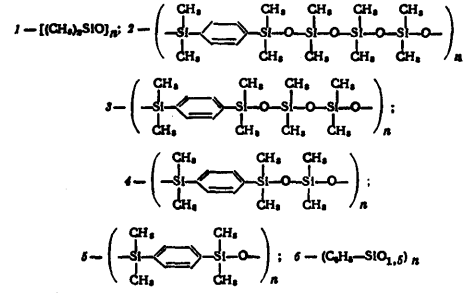


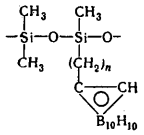
Figure 25. Isothermal thermogravimetric analysis of polysiloxanes[72]:



(Fig. 26) that the thermal stability of the benzoborimidazoline ring is lower than that of the imidazole ring.

Polymers containing carborane (barene) residues in the chain unit are extremely interesting[74]. Introduction of a carborane residue into a polymer molecule produces a considerable increase in thermal stability. Thus polyesters, polyamides, and other polymers obtained from dicarboxylic acids containing carborane ring systems are distinguished by exceptionally high thermal stability. The introduction of a carborane system into polysiloxanes produces

polycarboranesiloxanes having the structure



which show considerably better thermal stability than does polydimethylsiloxane[75]. Equally high thermal stability is characteristic of the polycarboranebenzimidazole

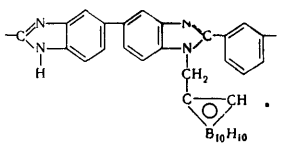


Table 10. Thermochemical and chemical stability of polyfluoroalkylsiloxanes[71].

Chain unit	Thermal stability on heating in sealed tube for 6 h: temp., °C	Thermal stability on heating in sealed tube for 6 h: polymer decomposed, %	Resistance to hydrolysis by 10% aq. NaOH 20°C
$[-Si(CF_2CHF_2)-O_{1,5}-]_n$	172	8	Si–C bond
	240	67	ruptured
$[-Si(CH_2CHF_2)-O_{1,5}-]_n$	170	14	ditto
	220	75	
$[-Si(CH_2CH_2CF_3)-O_{1,5}-]_n$	450	4	stable
	500	80	

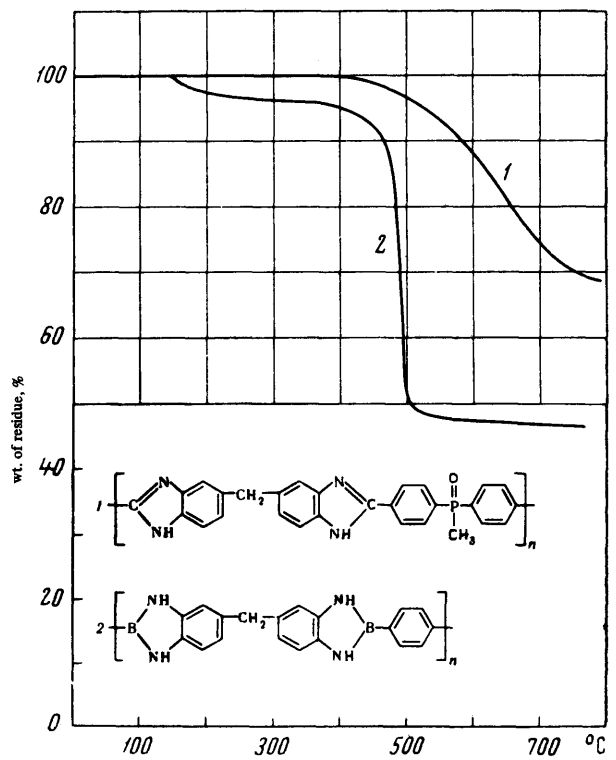


Figure 26. Dynamic thermogravimetric analysis (in nitrogen) of organoelementary polymers containing boron and phosphorus[77].

It surpasses the analogous unsubstituted polybenzimidazole in thermal stability, and when heated in the air to 900°C it loses only 25% of its original weight[76].

Very few phosphorus-containing polymers are characterised by high thermal stability. Among them are poly(phosphonitrile chloride) $[PCl_2=N]_n$ and PON polymers.

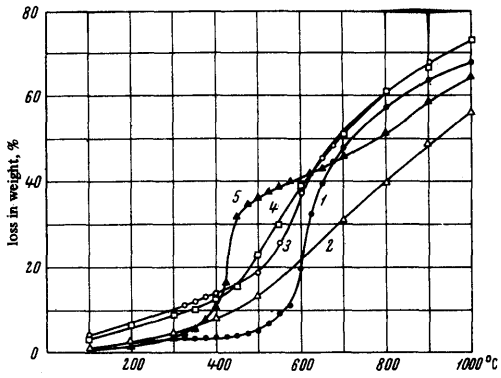


Figure 27. Relative thermal stability (determined by isothermal thermogravimetric analysis) of coordination polymers of bis-8-hydroxyquinol-6-ylmethane with the metals:
1) zinc; *2*) manganese; *3*) cobalt; *4*) nickel; *5*) copper.

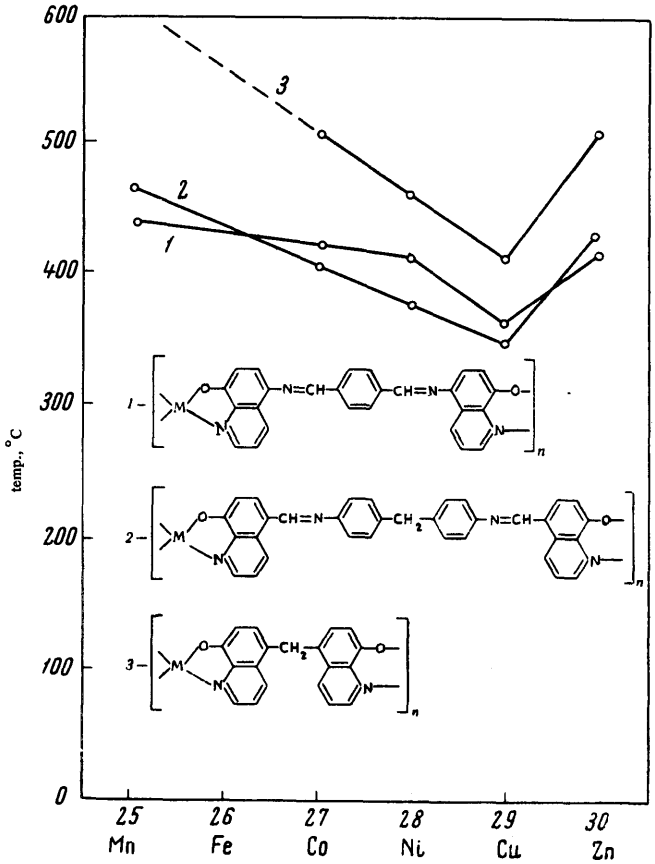
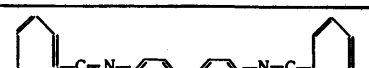
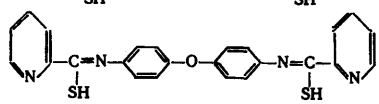
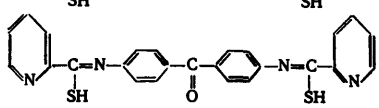
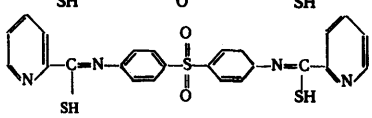


Figure 28. Dependence of decomposition temperature (thermal stability) of coordination polymers on atomic number of metal[79].

Table 11. Thermal stability of some coordination polymers[80].

Ligand	Metal	Loss in weight, %, at the temperatures (°C)								
		220	250	270	290	310	340	370	390	420
	Cu^{II}	2	1	1	decomp.	—	—	—	—	—
	Ni^{II}	0.3	0,1	0	0	0,2	6	decomp.	—	—
	Zn^{II}	0	0	0	0	0	0	0.5	0.2	decomp.
	Cu^{II}	0	0	2	2	3	decomp.	—	—	—
	Ni^{II}	0	0	0	0	0	0.5	3	decomp.	—
	Zn^{II}	0	0	0	0	0	0	0.5	3	decomp.
	Cu^{II}	0	0	0	0	2	decomp.	—	—	—
	Ni^{II}	0	0	0	0	2	decomp.	—	—	—
	Zn^{II}	0	0	0	0	0	0	0	0	decomp.
	Cu^{II}	0	0	0	1	3	decomp.	—	—	—
	Ni^{II}	0	0	0	3	0	decomp.	—	—	—
	Zn^{II}	0	0	0	0	0	0.2	0.3	0	decomp.

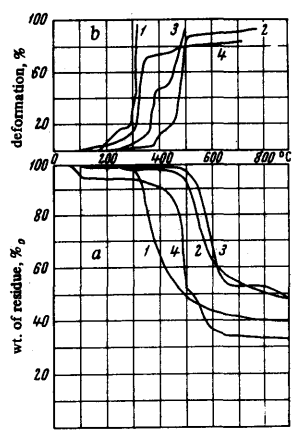


Figure 29. Thermal analysis[82]:
a) dynamic thermogravimetric analysis (heated in nitrogen at 4 deg min^{-1});
b) thermomechanical analysis of polydiphenylphosphinates of:
1) copper; *2*) zinc; *3*) cobalt; *4*) nickel.

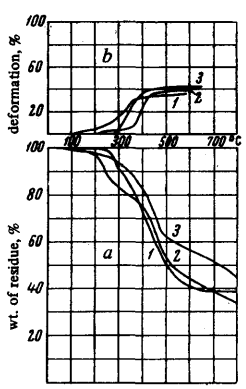


Figure 30. Thermal analysis of chromium polyphosphinates[83]:
a) dynamic thermogravimetric analysis (heated in air at 20 deg min^{-1});
b) thermomechanical analysis (with load of 100 g on tool of diameter 4 mm, heated in air at 70 deg h^{-1}):
1) polydiphenylphosphinate; *2*) poly-2,8-dimethylphenoxaphosphinate;
3) copolymer of equimolecular quantities of the two phosphinates.

Metal-containing polymers, especially inner-complex (chelate) polymers, are distinguished by high thermal stability. Inoy[78] determined the thermal stability of a series of coordination polymers of zinc, copper, nickel, cobalt, and manganese with bis-8-hydroxyquinol-5-ylmethane (Fig. 27). The dependence of the decomposition temperature (thermal stability) of several coordination polymers on the atomic number of the metal is shown in Fig. 28: the thermal stability of these polymers falls in the sequence Mn > Fe > Co > Zn > Ni > Cu. As is evident from Table 11, zinc gives the most thermostable coordination polymers, and copper the least stable[80].

The zinc complexes of salicylideneimines have also been shown to be the most stable[81]. This can be explained by the electronic structure of the bivalent ion of zinc, which possesses only one state of oxidation. Other transition metals can be oxidised to higher valencies, and this may catalyse processes of thermal decomposition.

The replacement of organic ligands by phosphinic acids enables coordination polymers to be obtained having an inorganic main chain. Such polymers are also characterised by high thermal stability, as is shown (Fig. 29) by thermomechanical and thermogravimetric analyses of copper, zinc, cobalt, and nickel polydiphenylphosphinates[82]. The nature of the metal ion plays an important part here. Cobalt polyphosphinate proved to be the most thermostable. The nature of the ligands is also significant, as is seen from Fig. 30, which illustrates the results of a dynamic thermogravimetric analysis of three chromium polyphosphinates[83]. The polydiphenylphosphinates proved to be more thermostable than the poly-2,8-dimethylphenoxaphosphinates.

IV. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF MACROMOLECULE

As we have seen from many examples, the structure of the chain unit in the macromolecule plays an immense part in determining the thermal stability of the polymer. However, besides the structure of the monomer unit, various structural features of the macromolecule itself often play a no less fundamental part in determining the thermal stability. Among such factors are regularity of structure of the macromolecule, isomerism of substitution in the ring, the presence of cross-links between macromolecules, and also the molecular weight. Below we shall examine one by one the effect of these structural features on the thermal stability of polymers.

1. Dependence of Thermal Stability on Regularity of Structure of Macromolecule

The chain units in a macromolecule can be arranged in two ways—"head to tail" $-CH_2.CHX.CH_2.CHX-$ or "head to head" $-CH_2.CHX.CHX.CH_2-$.

Vinyl polymers are usually built up in the first way, "head to tail". The content of units arranged in the second way is minute (1–2%). However, even a small number of units joined "head to head" may substantially affect the properties of the polymer, in particular its thermal stability.

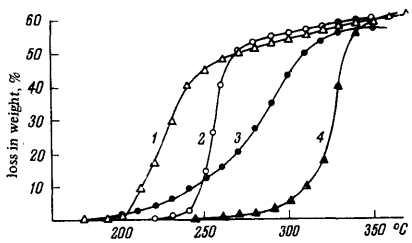
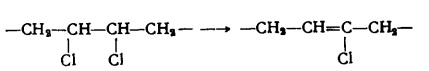


Figure 31. Isothermal thermogravimetric analysis of poly(vinyl chlorides) and poly(vinylidene chlorides) of various types[84].
1) poly(vinylidene chloride) of "head to tail" structure; *2*) poly(vinyl chloride) of "head to tail" structure; *3*) poly(vinyl chloride) of "head to head" structure; *4*) poly(vinylidene chloride) of "head to head" structure.

Murayama and Amagi[84] investigated the thermal breakdown of poly(vinyl chloride) and poly(vinylidene chloride) having head-to-head and head-to-tail structures. Fig. 31 shows that polymers having the latter type of arrangement begin to decompose at a great rate, and their decomposition extends as far as complete elimination of hydrogen chloride. In contrast to this, polymers with the head-to-head construction break down at a lower rate. The explanation is that, although the first stage occurs more easily owing to the lower stability of the head-to-head structure, the second stage occurs more slowly owing to formation of a chloroprene-like structure containing halogen attached to double-bonded carbon:



In this case there is no opportunity for a chain dehydrochlorination reaction to develop along the macromolecule.

2. Effect of Isomerism of Substitution in the Aromatic Ring

Polymers containing aromatic or heterocyclic rings in the chain differ substantially in thermal stability according to the relative arrangement of substituents in the ring.

Table 12 shows that polymers containing *para*-substituted rings are the most thermostable. Polymers containing the *meta*-isomers are less stable, as has been established with polyphenylenes, polyamides, and polybenzoxazoles. Derivatives of terephthalic acid surpass the corresponding derivatives of isophthalic acid in thermal stability.

In the case of aromatic heterocycles the relative arrangement of the heteroatoms also plays a significant part. Thus poly-1,2,4-oxadiazoles are less thermostable than are poly-1,3,4-oxadiazoles.

3. Effect of Lateral Groups and Branching

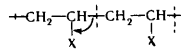
The presence of lateral groups and of branching in a macromolecule always leads to diminished thermal stability of the polymers. This principle is confirmed by comparing the relative thermal stabilities (T_h) of a series of polymers containing these structural features (Table 5).

The thermal stability of polyethylene (19)†, which is a branched-chain variety of polymethylene, is lower than that of the straight-chain polymer (22). The introduction of side-groups into every chain unit in the polymer lowers the thermal stability still more, as can be seen from the examples of polypropylene (16) and polyisobutylene (12). The same situation is observed on comparing poly(methyl acrylate) (10) with poly(methyl methacrylate) (3): the latter is inferior to the former in thermal stability.

A similar variation occurs in the perfluorocarbons, as is seen from the examples of polytetrafluoroethylene (25), polyperfluoropropylene (6), and polyperfluoroheptene (1). In this case the thermal stability also falls in the presence of side-groups, not only their presence but also their nature being significant: the larger the lateral group, the lower the thermal stability. Thus polyperfluoroheptene (T_h = 248°C) is less thermostable than is polyperfluoropropylene (297°C).

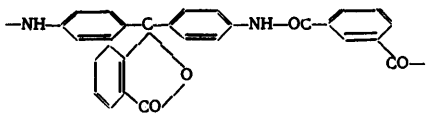
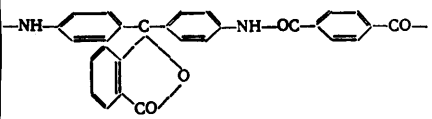
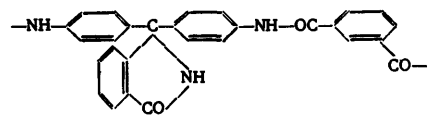
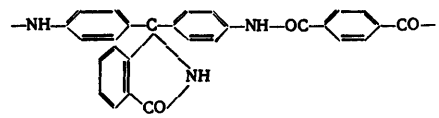
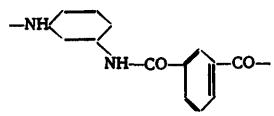
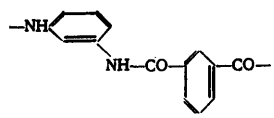
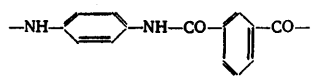
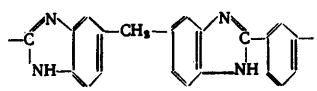
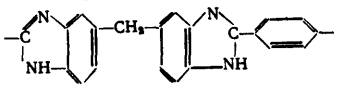
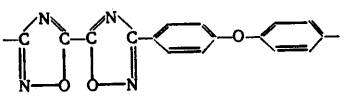
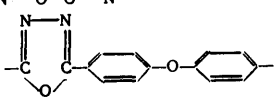
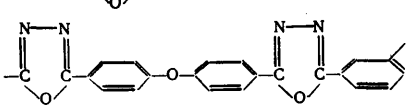
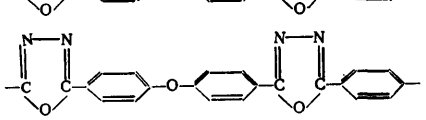
Substituents in the macromolecules of polyethers have an analogous effect: poly(propylene oxide) is less thermostable than is poly(ethylene oxide) (295° and 345°C respectively).

The presence of substituents in phenylene groups also lowers the thermal stability of polymers, as has been shown in the case of substituted poly-*p*-phenylene-ethylenes[17]. Thus polytetramethyl-*p*-phenylene-ethylene and poly-2,5-dimethoxy-*p*-phenylene-ethylene (265° and 375°C) are inferior in thermal stability to poly-*p*-phenylene-ethylene (430°C). In this case the number of substituents is also important. Thus the general rule can be formulated that the more substituents are present in a chain unit the lower is the thermal stability of the polymer. In the case of vinyl polymers this is because side-groups weaken the bonds between the chain units in the macromolecule, which facilitates their breakdown with the formation of monomer:



† The parentheses indicate the numbering of the polymers in Table 5.

Table 12. Thermal stability of isomeric polymers containing rings in the chain.

Polymer	Chain unit	Temp., °C	Ref.
Poly-*p*-phenylene		650*	17
Poly-*m*-phenylene		540*	17
Polyaniline-phthaleiniso-phthalamide		420**	85
Polyaniline-phthaleintere-phthalamide		450**	85
Polyaniline-imidophthalein-isophthalamide		420**	85
Polyanilineimido-phthaleintere-phthalamide		440**	85
Poly-*m*-phenyl-eneisophthal-amide***		330**	41
Poly-*m*-phenyl-eneisophthal-amide***		390**	41
Poly-*p*-phenyl-eneterephthal--amide***		410**	41
Poly-2,2′-*m*-phenylene-5,5′--dibenzimida-zolylmethane		490**	86
Poly-2,2′-*p*-phenylene-5,5′-dibenzimida-zolylmethane		500**	86
Poly-3,3′-*pp*′-phenoxyphenyl-ene-5,5′-bi-1,2,4,--oxadiazolyl		300**	87
Poly-2,5-*pp*′-phenoxyphenyl-ene-1,3,4-oxa-diazole		430**	65
Poly-5-*m*-phenyl-ene-1,3,4-oxa-diazol-2-yl-5′--*pp*′-phenoxy-phenylene-1′,3′,,4′-oxadiazol-2′-yl		380**	88
Poly-5-*m*-phenyl-ene-1,3,4-oxa-diazol-2-yl-5′--*p*′*p*″-phenoxy-phenylene-1,′3′,4′-oxadia-zol-2′-yl		430**	88

* Temperature at which a specimen loses half its weight during 2 h.
** Temperature of start of loss in weight on thermogravimetric curve.
*** Some of this information is obviously incorrect (Ed. of Translation).

4. Dependence of Thermal Stability on Degree of Cross-linking of Polymer

All the relations which we have considered hitherto have applied to linear macromolecules. However, there are also other structures, as is evident from Fig. 32. Linear chains may consist of (*a*) rings of spiran structure, or two linear polymer chains may be joined by cross-links, as in the case of (*b*) ladder polymers. Polymer chains joined to two adjacent chains in the same plane form (*c*) parquet structures, and finally chains joined to a large number of macromolecules arranged in all three directions form (*d*) spatially cross-linked three-dimensional structures. For the most part, bond formation between macromolecules leads in all the above cases to an increase in their thermal stability compared with that of the corresponding linear structure. Tessler[89] made a theoretical calculation showing that ladderlike structures form smaller quantities of volatile products during a given time than do analogous simple polymers.

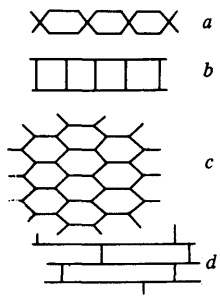


Figure 32. Various forms of macromolecules:
a) spiran; *b*) ladderlike; *c*) parquet; *d*) three-dimensional cross-linked.

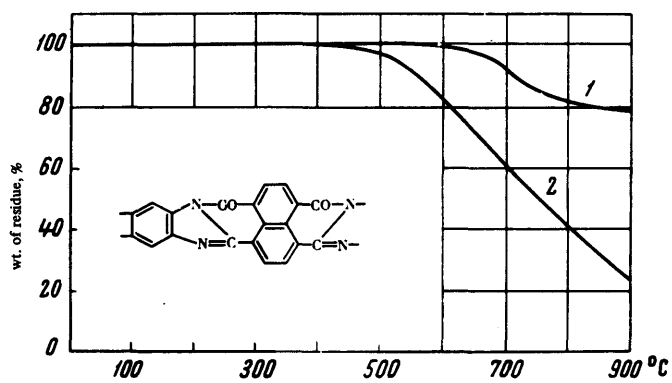


Figure 33. Dynamic thermogravimetric analysis (rate of heating 2.5 deg min^{-1}) of pyrrones[90] in:
1) nitrogen; *2*) air.

A dynamic thermogravimetric analysis of pyrrones shows (Fig. 33) that these ladderlike polymers have extremely high thermal stability. Such parquet structures as graphite, as well as porphyrin polymers, are characterised by exceptionally high thermal stability.

Cross-linked polymers have higher thermal stability because the introduction of cross-links increases the chemical stability of the polymers. A fundamental difference exists between the effect, on the properties of polymers, of interchain forces of interaction (both dipole forces and hydrogen bonds) and valency bridges: the former are strongly dependent on temperature, rapidly becoming weaker as the temperature rises, whereas the latter are independent of variation in temperature over a wide range.

Table 13. Temperature of half-decomposition T_h of styrene copolymers.

Content in copolymer, %			T_h, °C
styrene	divinyl-benzene	trivinyl-benzene	
100	0	0	364
98	2	0	365
75	25	0	373
75	0	25	393
0	100	0	399
44.2	55.8	0	401
0	0	100	462

Table 13 gives values of the thermal stability (T_h) for cross-linked copolymers of styrene with divinylbenzene and trivinylbenzene as a function of the frequency of cross-linking. Thus the cross-linking of chains has a considerable effect in raising the thermal stability, as is evident from the examples of polystyrene, polydivinylbenzene, and polytrivinylbenzene (364°, 399°, and 462°C respectively)[91-93].

This fact is illustrated by the thermogravimetric curves (Fig. 34) for polymers of divinylbenzene and trivinylbenzene and their copolymers with styrene. It is seen that the losses in weight of the trivinylbenzene polymers are smaller than those of the divinylbenzene polymers. The latter losses are in turn smaller than those of polystyrene. Fig. 35 shows comparative curves for the thermal stability of cross-linked polytrivinylbenzene and for several other polymers[92].

The strongly cross-linked polymer of 1,3,5-triacryloylhexahydro-1,3,5-triazine is a thermostable substance, decomposing at ~ 400°C.[94]

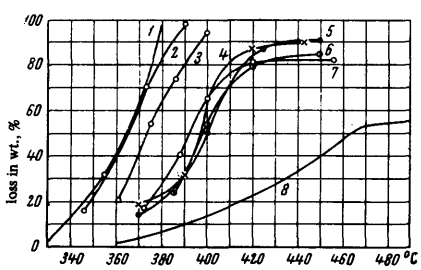


Figure 34. Relative thermal stability of polymers and their copolymers with styrene determined by isothermal thermogravimetric analysis[92,93]:
1) polystyrene; *2*) copolymer of styrene with 2% of divinylbenzene; *3*) copolymer of styrene with 25% of divinylbenzene; *4*) copolymer of styrene with 48% of divinylbenzene; *5*) copolymer of styrene with 55% of divinylbenzene; *6*) polydivinylbenzene; *7*) copolymer of styrene with 25% of trivinylbenzene; *8*) polytrivinylbenzene.

A marked improvement in thermal stability results from the formation of cross-links in polyarylates containing free hydroxyls in their macromolecule. Fig. 36 shows that a more thermostable polymer is formed by cross-linking such a polyarylate by means of maleic anhydride[95].

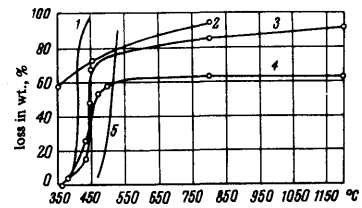


Figure 35. Relative thermal stability of polymers determined by isothermal thermogravimetric analysis[92]:
1) polymethylene; *2*) polyacrylonitrile; *3*) poly(vinylidene fluoride); *4*) polytrivinylbenzene; *5*) polytetrafluoroethylene.

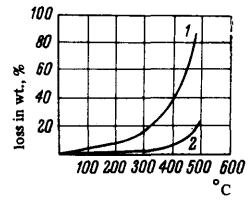


Figure 36. Thermogravimetric curves of polyarylates[95]:
1) original polyarylate D-5; *2*) polyarylate D-5 cross-linked with 15% of maleic anhydride.

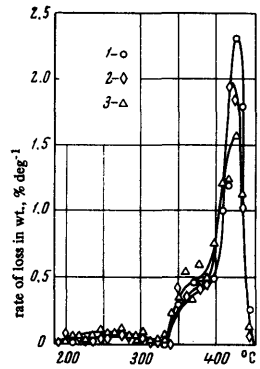
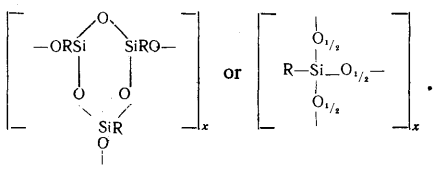


Figure 37. Differential thermogravimetric analysis of polyethylene exposed in air to different doses (Mrad) of radiation[96]:
1) 0; *2*) 5.2; *3*) 55.

The irradiation of polymers is a general method for cross-linking them and improving their thermal stability. Fig. 37 shows curves for the differential thermogravimetric analysis of polyethylene exposed in air to different doses of radiation[96]. It is seen that the thermal stability of the polymer increases with increase in the dose.

Andrianov[15] observed a marked increase in thermal stability as a result of the cross-linking of polyorganosiloxanes containing rings or irregular cross-links of the type

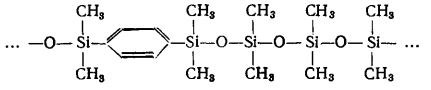


In this case the detachment of a chain unit or a large portion of the polymer molecule involves breaking the latter at three points, since the polymer contains cross-linked molecules. This is associated with the destruction of two or three energetically stable Si–O bonds. In polyorganosiloxanes containing three-dimensional bonds, therefore, no degradation of the molecular chains at a silicon–oxygen bond is observed even at 550°C, independently of the nature of the organic radical.

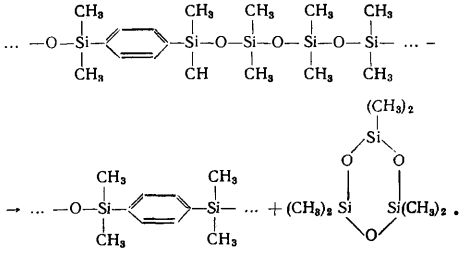
5. Effect of Copolymerisation

Copolymerisation or copolycondensation results in the formation of copolymers containing different types of unit in a chain. The presence of units differing in structure often presents difficulties in the detachment of molecules during thermal degradation.

A clear example of such improvement in thermal stability resulting from copolymerisation is provided by silaphenylene–siloxane copolymers having the structure



When such a polymer undergoes thermal breakdown, six-membered rings are split off:



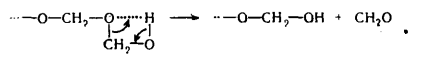
This process extends along that part of the chain which consists of dimethylsiloxane units. When a silaphenylene group is reached, however, ring formation becomes impossible, and degradation ceases. Therefore the thermal stability of such copolymers is considerably higher than that of polydimethylsiloxanes (temperatures at which breakdown begins 450° and 350°C respectively).

An analogous improvement in thermal stability is observed in copolymers of formaldehyde with cyclic oxides or acetals[97]. Polyformaldehyde itself already decomposes at 170°C, whereas its copolymers are stable up to 200°C.

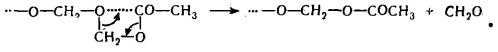
6. Effect of Other Structural Features on Thermal Stability

Several structural features of polymers, other than those which we have discussed, affect their thermal stability. We must first note the part played by end-groups.

It has been shown in the case of polyformaldehyde that its thermal stability depends on the nature of the terminal groups. Thus ordinary polyformaldehyde, having hydroxyls at the ends of the macromolecules, begins to decompose at about 170°C.[98] Acetylation yields a stabilised polyformaldehyde containing acetyl groups at the ends of the chain. The breakdown of polyformaldehyde takes place by a chain mechanism, beginning at the end-groups:



Acetylation changes the nature of the terminal group, and depolymerisation proceeds according to the equation



The acetyl group, being heavier and less mobile, requires more energy for its transfer, and therefore such acetylated polyformaldehyde decomposes at a higher temperature (200°C). Fig. 38 illustrates the results of a thermogravimetric analysis of polyformaldehyde in a vacuum, showing the higher thermal stability of acetylated polyformaldehyde[99].

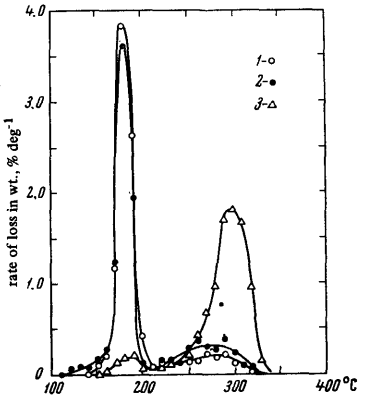


Figure 38. Differential thermogravimetric analysis of polyformaldehyde heated in a vacuum at different rates (deg min^{-1})[99]: *1*) polyformaldehyde (1); *2*) polyformaldehyde (0.5); *3*) acetylated polyformaldehyde (1).

In some cases the glass point and the thermal stability of polymers are also interrelated. If the glass point lies far below the temperature of decomposition, no relationship between them is observed, and the thermal stability is determined by the energies of the interatomic bonds. If, however, the glass point lies above or near the decomposition point, there is a clear relation between them: in these cases thermal breakdown is usually considerably accelerated after transition through the glass point.

---o0o---

The data given above show that we are now aware of several relations linking the thermal stability of polymers with their chemical structure. Among a number of structural features having general significance and producing high thermal stability in polymers the most important are

high interatomic bond energies, the presence of stable aromatic and other groupings in the chain unit, the presence of intermolecular bonds, ladderlike, and other cross-linked structures.

High energy of the bonds between chain units, as also within a unit and with surrounding groups, constitutes an important factor determining the thermal stability of a polymer. It makes difficult the formation of free radicals, by either thermal or thermo-oxidative mechanisms, and prevents the occurrence of chain reactions of thermal and oxidative degradation. An effective way of producing thermostable structures is to introduce aromatic carbocycles and heterocycles, as well as carborane, ferrocene, and other stable groups. Improvement in the thermal stability parallels the increased content of aromatic rings in the chain. Decreasing the content of aliphatic groups, both in the chain and in side-groups, and increasing the content of aromatic rings in the polymer are of fundamental value. The thermal stability is improved in all cases on passing to ladderlike, parquet, and three-dimensional cross-linked structures, this being due to the diminished opportunities for the formation of volatile pyrolysis fragments. One way of improving the thermal stability of vinyl, oxide, and other linear polymers is to diminish their capacity for depolymerisation, this being accomplished by introducing large end-groups and by copolymerisation with monomers giving stable chain units, incapable of easy detachment as monomeric molecules.

An important way of improving thermal stability is to introduce, into the composition of the polymer, groups which are able to increase its resistance to oxidation or pyrolysis, as occurs in the case of "self-protective" polymers. The incorporation of groups which prevent oxidation or pyrolysis by combining with the free radicals formed and thus terminating the chain processes of decomposition considerably enhances the thermal stability of polymers. Such protective groups are sometimes formed in the course of chemical rearrangement of the polymer, but far more often they are introduced as "external" additives (stabilisers, antioxidants, etc.), which is a very widely used technical procedure for improving stability during the processing of polymers.

As is evident from the data which have been discussed, several relations have already been established linking the structure of polymers with their thermal stability. The task for future research is to refine these relations, so that they can be used still more widely for the consciously controlled synthesis of thermostable polymers.

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Synthesis of Vinyl Ethers Containing Functional Groups and Heteroatoms

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The paper gives a brief analysis of the chief methods for synthesising vinyl ethers containing functional groups and heteroatoms. Published information on the Favorskii-Shostakovskii reaction—the direct vinylation of hydroxylated compounds (alkoxyalkanols, glycols, polyhydric alcohols)—is surveyed, the mechanism of the reaction is discussed, and its application considered to the vinylation of nitrogen-containing alcohols (amino-alcohols and amino- and nitro-phenols), and to alkylthio-alcohols, silicon-containing alcohols, halogenated alcohols, and halogenated phenols. The elimination of hydrogen halides from halogenated ethers and the reaction of vinyl exchange are also reviewed. Methods are discussed based on the reactions of functional groups in substituted vinyl ethers (vinyloxyalkanols and halogenated and nitrogen-containing vinyl ethers), catalytic elimination in functional acetals, and the interaction of halogenated acetals with metals and of alkoxides of functional alcohols with vinyl halides. The fields of application of each of the above methods are assessed. A list of 302 references is included.

CONTENTS

I.	Introduction	907
II.	The Favorskii-Shostakovskii reaction	907
III.	Elimination of the elements of a halogen halide from halogenated ethers	911
IV.	Vinyl exchange	912
V.	Syntheses of vinyl ethers based on the reactions of functional groups in substituted vinyl ethers	912
VI.	Catalytic elimination in a series of functional acetals	914
VII.	Other methods	915

I. INTRODUCTION

The increasing amount of research on $\alpha\beta$-unsaturated ethers containing reactive functional groups has long ago made it necessary to summarise and analyse in detail the available experimental information. A monograph[1], review papers[2-6], and numerous theses[7-21] from the Favorskii–Shostakovskii school have covered more or less fully only the vinyl ethers of alcohols containing no functional substituents. The present paper gives a brief analysis of the principal methods for the synthesis of functional vinyl ethers, and an attempt is made as far as possible to assess the field of application of each of them. Alkoxyethylenes containing substituents in the vinyl group, vinyl sulphides, and vinylamines are not discussed.

II. THE FAVORSKII–SHOSTAKOVSKII REACTION

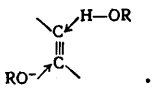
Direct vinylation, i.e. the addition of hydroxylated compounds to acetylene in the presence of basic catalysts (the Favorskii–Shostakovskii reaction[22,23]), is at present the most widely used method for preparing vinyl ethers. The simplicity of the synthesis, its completion in one stage, the availability of the starting material, and the almost quantitative yields of the required products make this a convenient method for industrial application. An obstacle to its wide introduction into industry is the need to use high pressures in individual cases: this, of course, increases the likelihood of explosion of the acetylene[24], but the danger is often greatly exaggerated[25].

The work of the Favorskii–Shostakovskii school[1,23,26-30] had already demonstrated by the end of the 1930s, independently of Reppe's work[31,32], the possibility of accomplishing industrial syntheses based on acetylene under pressure. In contrast to the patents of the IG. Farbenindustrie AG.[33-35], which envisaged dilution of the acetylene with an inert gas, a more intensive technology was developed in the USSR, under conditions of the inevitable dilution of the acetylene with the vapours of the starting material to be vinylated and the vinyl ethers formed, which are reliable stabilisers.

1. Mechanism of the Reaction

In spite of isolated attempts to make the problem a matter of controversy[36,37], the view has become accepted, strengthened by chemical kinetic data[38-40], that the process is a typical case of nucleophilic addition at the triple bond[41,42]. Vinylation has already been cited[43] as a classic example of nucleophilic addition to acetylenic systems. Nevertheless, examples exist[44,45] which do not fit well into such a scheme.

A detailed examination of the mechanism of vinylation has recently been made in a review[41] and in theses[18,21,46]. However, several aspects of the problem have been left untouched. Nucleophilic vinylation can be interpreted most acceptably as a concerted *trans*-addition:



This scheme[47] explains perfectly satisfactorily the main features of vinylation—(*a*) preferential formation of *cis*-adducts[38,41], (*b*) oriented addition to monosubstituted acetylenes, with formation of β-isomers when an acceptor substituent (phenyl[38,42,48], trifluoromethyl[49], diethoxymethyl[50]) is present at the triple bond, and formation of the α-isomer if acetylene containing a donor substituent is involved in the reaction[50], (*c*) the difficulty of reaction when donor substituents are present at the triple bond[51], and (*d*) increase in rate of reaction with increase in the nucleophilic character of the reagent[40,44,52]. In cyclic mechanisms *cis*-addition is assumed, although there has probably not yet been an example of the isolation of *trans*-adducts, which should be formed in this case.

Analysis of the literature in terms of simultaneous nucleophilic addition permits us to explain tentatively several known generalisations and discrepancies associated with vinylation which hitherto have not been entirely clear. Thus the presence of water sharply diminishes the rate of vinylation of aliphatic alcohols[1,4,26], whereas it definitely promotes the vinylation of phenols[40,44,52] and thiols[53,54]. In the absence of solvents or in non-polar media, phenols yield vinyl ethers under considerably more severe conditions than do aliphatic alcohols[37,46]. Yet in the vinylation of phenols in an alcoholic medium, under conditions close to those used for the vinylation of aliphatic alcohols, the corresponding aryl vinyl ethers are formed smoothly[55]. In all these cases a number of acid–base equilibria (alcohol, water, alkali, alkoxide) are superposed and actively interact. In the pair alcohol–water the latter component is a stronger acid than the alcohol, and suppresses dissociation thereof; at the same time the undissociated alcohol molecules act as a base towards the water, displacing the equilibrium towards formation of hydroxide ions. The net result is that the concentration of alkoxide ions and the rate of addition of alcohol to acetylene fall. The accompanying absorption of acetylene which is observed in several cases is probably due to "vinylation" of water[36,40]. Another secondary reaction involving water,

$$HC{\equiv}CH + H_2O + NaOH \rightarrow CH_3COONa + H_2:$$

is known[56]. According to a patent[57] almost pure hydrogen and sodium acetate in 96% yield can be obtained in this way.

Towards phenol water acts as a base and an ionising agent: it intensifies dissociation of the phenol, thereby increasing the concentration of phenoxide ions, which ultimately facilitates vinylation. Alcohols are also capable of filling the function of water as an ionising agent and a proton-acceptor in the vinylation of phenols[40,53-55]. In our view a similar explanation can be put forward for the favourable influence of water and alcohols in the vinylation of thiols[40,53-55,58] and also for the possibility of using t-butyl alcohol as the medium in the vinylation of alcohols[39]. The favourable influence of dioxan and *N*-methylpyrrolidone on vinylation[59] is probably due primarily to their increased ability to dissolve acetylene; however, being strong proton-acceptors, these solvents should further also strengthen the acid–base dissociation of the substrate.

The rate of vinylation falls appreciably on passing from a primary to a tertiary alcohol[10,60,61]. Since the nucleophilic character of alkoxide ions increases in the same sequence, this observation appears at first glance to contradict the mechanism of nucleophilic vinylation. This is seemingly not only a matter of steric hindrance to activation. According to the scheme of concerted addition, the rate of vinylation depends both on the nucleophilic character of the alkoxide ion and on the ability of the medium to donate protons. The latter is known to fall from a primary to a tertiary alcohol.

Although the above mechanism of simultaneous *trans*-addition provides an acceptable explanation for most of the features of nucleophilic vinylation, nevertheless it is probably an extremely crude approximation, and cannot claim to be universally applicable. In particular, it is difficult with its aid to provide any satisfactory explanation of the known dependence of the reaction velocity on the cationic portion of the catalyst[40,45] (though this applies to all other mechanisms of vinylation). It has been suggested[40] that nucleophilic attack at the triple bond is preceded by attack by the cation with formation of an "acetylene–cation" complex compound. In any case, it is now clear that all the variety of modifications and variants of the reaction of vinylation cannot be forced into the framework of any one scheme.

2. Field of Application

In principle the reaction does not extend merely to those functionally substituted alcohols and phenols which contain structural units sensitive to alkalis and to heat. Compounds which have not yet proved susceptible to direct vinylation include in particular unsaturated aliphatic alcohols (the higher unsaturated alcohols possibly constitute an exception[62]). The main reason preventing direct vinylation in unsaturated alcohols may be supposed to be their prototropic isomerisation into the corresponding carbonyl compounds. In a kinetic study[45] of the vinylation of allyl alcohol (together with other alcohols) in the presence of sodium hydroxide as catalyst, the reaction velocity was measured from the absorption of acetylene, but it is not clear whether allyl vinyl ether was isolated in the pure form. The vinylation of the but-2-enyl and allyl monoethers of ethylene glycol[63] is apparently not accompanied by isomerisation of the radical. Tertiary ethylenic alcohols, with which the final stage of isomerisation (conversion into the α-ethylenic alcohol, and then into a carbonyl compound) is excluded, can probably be vinylated under the conditions of the Favorskii–Shostakovskii reaction with preservation of the molecular skeleton. In general, of course, the position of the double bond need not necessarily be maintained here. In this connection patent information[64] on the preparation of the vinyl ether of *p*-menth-1-en-8-ol (together with the vinyl ethers of other mono- and poly-cyclic terpene alcohols) by vapour-phase vinylation over basic catalysts is not without interest. In the case of acetylenic alcohols isomerisation may be supplemented by intramolecular and intermolecular "self-vinylation".

3. Alcohols having Oxygen-containing Functions

(*a*) Alkoxyalkanols. Alcohols containing alkoxy-groups (monoethers of glycols) are smoothly vinylated under ordinary conditions with the formation of alkoxyalkyl vinyl ethers[4,63,65,66]. Monoalkyl ethers of hydrobenzoin have been successfully vinylated[67-69]. Furfuryl vinyl ether has been obtained[70] in 45% yield by the vinylation of furfuryl alcohol in aqueous medium; the reaction is more successful in the absence of solvents (yield of the ether 68.7%[71]). The presence of water proved necessary in the vinylation of guaiacol[72] and other alkoxyphenols[73].

(*b*) Glycols. In the vinylation of 1,2- and 1,3-glycols, cyclic acetals[74,75]—products of the isomerisation[76] of monovinyl ethers—are usually present in the reaction mixture. The vinylation of ethylene glycol is accompanied[23] by the formation of other unsaturated products, boiling at 150–195°C, of undetermined structure. However, this has not been confirmed in later investigations. With propyne[77] ethylene glycol gives exclusively 2,4-dimethyl-1,3-dioxolan under the conditions of vinylation.

A patent stated[78] that vinyl ethers of ethylene glycol could be obtained by passing a mixture of acetylene and the glycol vapour over heated metals (calcium, magnesium, barium, copper, aluminium), peroxides, or salts on carriers. The preparation was reported[33,34] of vinyl ethers of glycols (the monovinyl ether of ethylene glycol and the

divinyl ethers of ethylene, diethylene, and triethylene glycols) by the action of acetylene diluted with an inert gas on the diols in the presence of alkaline catalysts under pressure. Vinylation forms the basis of a process for the manufacture of the divinyl ether of butane-1,4-diol[4,79]. The synthesis of the divinyl ether of triethylene glycol has been described in a thesis[12]. A process which has been patented[80] for the production of monovinyl ethers of ethylene glycol, trimethylene glycol, and diethylene glycol is based on the rapid removal of the resulting ethers from the reaction zone by means of excess of acetylene or an inert gas. Shostakovskii et al.[81] accomplished the synthesis of the monovinyl ethers of ethylene, propylene, tetramethylene, diethylene, and triethylene glycols under pressure. The vinylation of butane-1,4-diol in tetrahydrofuran gives a 52% yield of the monovinyl ether[82]. Monovinyl ethers can be obtained[83] by vinylating glycols in the liquid phase at normal pressure and a temperature of 100°C with simultaneous removal of the reaction products. Some information has been published[45] on the kinetics of the vinylation of butanediol and diethylene glycol. The synthesis of vinyl ethers of diethylene glycol has been discussed also by Zimmerman et al.[84]

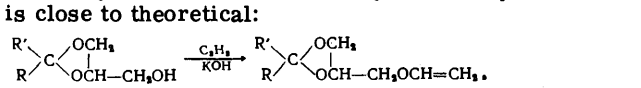
Qualitative assessment indicates that ease of vinylation increases in the sequence from ethylene glycol through diethylene glycol to triethylene glycol[85]. The exhaustive vinylation of triethylene glycol yields as secondary products vinyl ethers of ethylene and diethylene glycols and also 2-methyl-1,3-dioxolan. The vinylation of diethylene glycol is accompanied by the formation of vinyl ethers of ethylene glycol and 2-methyl-1,3-dioxolan. These facts indicate cleavage of the ether bonds during the reaction. Acetylene probably plays an active part in this secondary process. During the vinylation of diethylene glycol partial conversion of the monovinyl ether into an eight-membered cyclic acetal has been noted[86].

A simple apparatus has been developed[87] for the continuous preparation of vinyl ethers of glycols at atmospheric pressure. Continuous synthesis of acetaldehyde is accomplished by subsequent hydrolysis of the vinylation products. This scheme forms the basis of a new industrial method for manufacturing acetaldehyde via the vinyl ethers[88-91]. An interesting and successful attempt has been made to produce vinyl ethers (including those of glycols) by the direct use—instead of free acetylene—of calcium carbide in aqueous medium[92,93] under conditions of alkaline catalysis. A process for preparing the divinyl ethers of quinol, resorcinol, catechol, and trimethylquinol has been investigated[94]. The mono- and di-vinyl ethers of hydrobenzoin and isohydrobenzoin[69,95,96] and of anthraquinol[97] and the divinyl ether of bishydroxyphenylpropane[98] have been obtained.

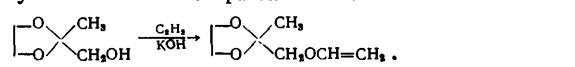
(*c*) Polyhydric alcohols. The early work on the vinylation of glycerol showed[23,75,99] that the yields of mono- and di-vinyl ethers could be controlled by varying the concentration of acetylene, and with excess of the latter exhaustive vinylation could be accomplished. The authors assumed that under these conditions the trivinyl ether of glycerol could be obtained in 90% yield. Subsequent refinement of these investigations by Shostakovskii et al.[20,21,100] has established, however, that a substance which is formed under these conditions in ~ 63% yield is actually 2-methyl-4-vinyloxymethyl-1,3-dioxolan, while the yield of the trivinyl ether of glycerol does not exceed 10%. American workers have reached a similar conclusion[59]. They synthesised the trivinyl ether of glycerol in up to 50% yield by a special method[59] ensuring a considerable excess concentration of acetylene in the reaction zone and brief contact between the reactants, *N*-methylpyrrolidone being used as solvent. The vinylation of glycerol has been accomplished in dioxan with the use of a three- to four-fold excess of acetylene in the presence of potassium butoxide[20,21,100]. Under these conditions 2-methyl-4-vinyloxymethyl-1,3-dioxolan and the trivinyl ether of glycerol were obtained in 43% and 25–28% yields respectively. The mono- and di-vinyl ethers of glycerol could not be isolated. Preparation of a monovinyl ether of glycerol has been reported[4,75], as also that of monoalkenyl ethers of glycerol[101,102].

The first communication on the vinylation of pentaerythritol and trishydroxymethylethane was made by Atavin[103]. In the latter case[104] 5-hydroxymethyl-2,5-dimethyl-1,3-dioxan, 2,5-dimethyl-5-vinyloxymethyl-1,3-dioxan, and 2,2-bisvinyloxymethylpropanol were isolated. Under the same conditions a diacetal and 2-methyl-5,5-bisvinyloxymethyl-1,3-dioxan were obtained from pentaerythritol[105]. A 22% yield of a divinyl ether of pentaerythritol has been synthesised in aqueous medium[106]; further vinylation of the product in the absence of water yielded a tetravinyl ether (60–70%) and 2-methyl-5,5-bisvinyloxymethyl-1,3-dioxan (30–40%). On vinylating pentaerythritol in alcohol, only a tetravinyl ether was isolated[107].

(*d*) Partial ethers of polyhydric alcohols. The vinylation of 1-alkoxypropane-2,3-diols[20,21,108] gives 4-alkoxymethyl-2-methyl-1,3-dioxolans and 1-alkoxy-2,3-divinyloxypropanes. 2,2-Dialkyl-4-hydroxymethyl-1,3-dioxolans are vinylated at a lower temperature (110–120°C) than are monohydric alcohols[109]. The yield of vinyl ethers is close to theoretical:



Several compounds of this type have been reported previously without detailed description[4-6]. Cyclic ketals of acetol are vinylated without complication[110]:



The preparation of mono-, di-, and tri-vinyl ethers of cellulose has been reported[111]. Subsequently only the corresponding acetals could be isolated[112] on vinylation of the same carbohydrate. Recently cellulose has been vinylated in aqueous dioxan[113]. Tetrahydrofuran was used as solvent for the vinylation of starch[114]. Vinylation of mannitol[115] gave only a low yield of its triacetal. A 10 to 15-fold excess of acetylene is necessary in order successfully to suppress isomerisation during the vinylation of polyhydric alcohols[116]. In this way a tetravinyl ether of α-methylglucoside and vinyl ethers of cellulose were obtained in yields of 65–80%. The vinylation of mono- and di-acetyl derivatives of α-glucose, α-galactose, mannitol, sorbitol, and dulcitol has been accomplished. In all cases it was reported that the completely vinylated ethers were isolated[117]. When acetylene reacts with poly(vinyl alcohol)[118] in aqueous alkali, not more than 6 mole % of the hydroxyls are etherified.

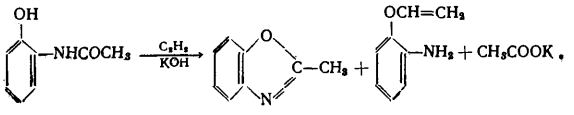
(*e*) Alcohols having other oxygen-containing functions. Very brief mention has been made[4,6] of the production of vinyl ethers of partial acetates of ethylene glycol and glycerol in the presence of salts of organic acids. The yields are not given, the boiling point serving as the only characteristic of the ethers. The reaction is accompanied by active redistribution of acyloxy-groups. Among hydroxy-compounds having other oxygen-containing functions, phenolic ketones have been successfully

vinylated[98]. The reaction conditions are analogous to the synthesis of the vinyl ethers of alkylated and arylated phenols[119,120]. Naphthyleneglycollic acid is converted[121] under conditions of vinylation into a mixture of mono- and di-vinyl ethers, the latter of which has been obtained also directly from acenaphthenequinone.

4. Nitrogen-containing Alcohols

(*a*) Amino-alcohols. Vinyl ethers of hydroxyethylamines have been obtained[31-35] in the presence of basic catalysts at 80–250°C. The conditions for the vinylation of aliphatic alcohols are too severe[122,123] for aminoalkanols. The best results are obtained by conducting the reaction in benzene, with an alkoxide of the corresponding alcohol as catalyst. Complete and partial vinyl ethers of bis- and tris-hydroxyethylamines have been synthesised[124]. An apparatus in which a gas–liquid emulsion is produced by means of a stirrer has been proposed[125] for the preparation of trisvinyloxyethylamine. In such apparatus vinylation can be conducted over a wide range of pressures (2–12 atm). Decrease in pressure and the presence of moisture impair the yields of vinyl ethers. Kinetic investigations (with bis-2-hydroxyethylamine in t-butyl alcohol and an initial acetylene pressure of 19.5 atm)[44] indicate that the order of the reaction with respect to the amino-alcohol varies from the first to zero as the concentration of the latter changes. Methods in the mathematical planning of experiments have been used in the kinetic study of the vinylation of trishydroxyethylamine[126]. The vinylation of phenylaminoethanol in the presence of caustic potash in butanol yields phenylaminoethyl vinyl ether[4]; under similar conditions but in the presence of cadmium acetate[127] *N*-phenyloxazolidine is formed.

(*b*) Aminophenols. Various aminophenols[128-133] and hydroxydiphenylamines[132,134] have been subjected to vinylation, the expected vinyl ethers being obtained in all cases. Vinylation is promoted by the presence of 15–20% of water based on the weight of the aminophenol[128]. The corresponding vinyl ethers have been synthesised by the vinylation of phenolic acetanilides[135], the reaction being effected in dioxan medium in the presence of 20–25% of caustic potash. The vinyl ether of *o*-hydroxyacetanilide was not isolated, owing to cyclisation and saponification of the original phenol:



(*c*) Nitrophenols. The possibility of the direct vinylation of *p*-nitrophenol was probably first shown in a kinetic study[40] of the vinylation of substituted phenols. The preparative vinylation of *o*-, *m*-, and *p*-nitrophenols is accomplished[136,137] in aqueous dioxan in the presence of cadmium acetate. Caustic potash and zinc acetate proved to be less effective catalysts (the yield of ethers did not exceed 2.5–3.5%). The *para*-isomers are most readily vinylated (at 145–150°C), the successful vinylation of *m*- and *o*-nitrophenols requiring temperatures of 175–185°C. Halogenated nitrophenols (2-chloro-4-nitrophenol, 2,6-dichloro- and 2,6-dibromo-nitrophenols) require temperatures of at least 180°C for vinylation, this being due[136] to steric hindrance by the *ortho*-substituents.

5. Mercapto- and Alkylthio-alkanols

Shostakovskii et al.[138] investigated the reaction between acetylene and 2-mercaptoethanol, and obtained a 70–75% yield of 2-vinylthioethanol, which clearly illustrates the greater reactivity of the thiol group than of hydroxyl towards vinylation:

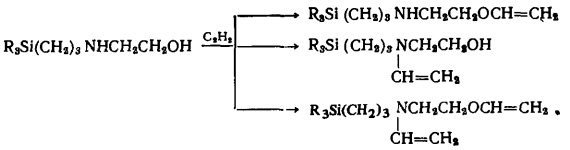
$$HOCH_2CH_2SH + C_2H_2 \xrightarrow[90-105^\circ]{20\%\ KOH} HOCH_2CH_2SCH{=}CH_2.$$

Further vinylation under more severe conditions (120 to 135°C) yields the diether.

The vinylation of 2-ethylthioethanol[139] gave a 40–60% yield of ethylthioethyl vinyl ether. The vinylation of thiodiglycol[140,141] involves complications, and only partly follows the usual scheme: there is a very vigorous competing process, yielding vinyl ethers of 2-mercaptoethanol. Experiments in the absence of acetylene, under otherwise similar conditions, did not yield such ethers. This proves that their formation was not a consequence of dehydration of the thiodiglycol. It is possible that acetylene plays an active part in cleaving the carbon–sulphur bond. It is not excluded that rupture of this bond during vinylation is common to 2-hydroxyalkyl sulphides, although work on the vinylation of 2-ethylthioethanol[139] and 2,2-dialkylthiopropanols, in which only the normal reaction products were isolated[142], would appear not to support this hypothesis. The vinylation of 1-thienylcarbinols in dioxan in the presence of potassium hydroxide yields the corresponding vinyl ethers[143].

6. Silicon-containing Alcohols

γ-Organosilicon alcohols can be vinylated[145] by the Favorskii–Shostakovskii method. The highest yields (65–68%) are obtained[146] at 150–160°C and acetylene pressures of 15–20 atm in the presence of potassium ethoxide. Under these conditions tertiary γ-silicon-containing alcohols are not vinylated[147]. Ethylenic and acetylenic tertiary γ-silicon-containing alcohols are cleaved at the SiC≡C bond during the reaction, with the formation of hexaalkyldisiloxanes. The vinylation of α- and β-silicon-containing alcohols in the presence of potassium hydroxide and alkoxides entails breakdown of the initial compounds[147]. Trialkylvinyloxysilanes can be obtained by vinylating trialkylsilanols[148] in the presence of potassium silanoxide in dioxan medium at 65–70°C. The vinylation of trialkylsilylpropylaminoethanols[149] yields three different products:



In view of the reported[5] unsuccessful attempts at the vinylation of primary and secondary aliphatic amines, the structures of the latter two products perhaps require refinement.

7. Halogenated Alcohols and Phenols

The literature probably contains no example of the direct vinylation of halogenated alcohols: the obstacle is their sensitivity (especially of 1,2- and 1,3-halogenohydrins) to the action of bases. An exception is 2,2,2-trifluoroethanol, which is 90% converted into the vinyl ether

on being vinylated (17% potassium hydroxide at 135–150°C for 10 h) under pressure in an autoclave[150].

Halogenated phenols undergo vinylation without appreciable complication[151,152]. The vinyl ethers of monochloro-(fluoro)-, 2,4-dichloro-, 2,4,6-trichloro-, pentachloro-, and pentafluoro-phenols have been obtained in good yields[153]. Replacement of caustic potash by zinc acetate permitted the synthesis also of the vinyl ethers of 2,4,6-tribromo- and chloronitro-phenols, these phenols being unstable in an alkaline medium. The vinyl ethers of *o*-chloro-, *p*-chloro-, 2,4-dichloro-, 2,4,6-trichloro-, and pentachlorophenols have been prepared[4] by vinylation with acetylene diluted with nitrogen in the presence of zinc and cadmium acetates. The ability of halogenated phenols to undergo vinylation is directly dependent on their acidity[151,152]: fluorophenol is most easily vinylated, and bromo- and chloro-phenols with greater difficulty. These results contradict kinetic data[39,154], and are probably explained by the differing stability of phenols under the conditions of vinylation.

III. ELIMINATION OF THE ELEMENTS OF A HALOGEN HALIDE FROM HALOGENATED ETHERS

In spite of the greater lability of halogen in 1-halogenoethyl ethers (substitution and detachment takes place by a unimolecular mechanism) and the relative accessibility[155,156] of these compounds, they are considerably more rarely used than are 2-halogenoethyl ethers for the synthesis of functional ethers, owing to their instability. The vinyl ethers of allyl and prop-2-ynyl alcohols have been obtained[157] in this way, as also those of mono- and di-methylethynylcarbinols. The effectiveness of the scheme

$$CH_3CH(OR)_2 \xrightarrow{BCl_3} CH_3CHClOR \xrightarrow{(CH_3)_3N} \left[\begin{array}{l} CH_3CHOR \\ \quad | \\ \quad +N(CH_3)_3 \end{array}\right] Cl^- \xrightarrow{100-120^\circ C} CH_3{=}CHOR + N(CH_3)_3 \cdot HCl$$

is due to the use of boron trichloride at the stage of formation of the α-chloro-ether. 2-Chloroethynyl vinyl ether is formed[158] when 1,2′-dichlorodiethyl ether is heated in diethylaniline at 80–85°C. 1-Bromo-2-vinyloxyethylene has been prepared[158] under similar conditions:

$$CH_3CHClCHBrCH_2Br \rightarrow CH_2{=}CHOCH{=}CHBr.$$

α-Silicon-containing vinyl ethers have been obtained[159] by dehydrochlorination of 1-halogenoethyl ethers of the corresponding alcohols:

$$R_3SiCH_2OCHClCH_3 \xrightarrow{-HCl} R_3SiCH_2OCH{=}CH_2.$$

Conditions for the dehydrohalogenation of 2-halogenoethyl ethers have been discussed in detail in a monograph[156]. The reaction goes with considerably greater difficulty than in the cases of 3-halogenoalkyl ethers and alkyl halides. The 2-halogenoethyl ether is usually distilled over excess of solid caustic potash or caustic soda. The peculiar resistance of β-halogeno-ethers to dehydrohalogenation deserves more than mere mention. The process is undoubtedly bimolecular, so that the main factor here is not the lability of the halogen, which has hitherto been stressed[156], but that of the α-hydrogen atom (with respect to the oxygen), which is the primary object of attack by the nucleophile. In view of the polarity of the $O{\leftarrow}C^{\delta+}$ bond, detachment of a proton from the OCH_2 group should apparently be facilitated, whereas actually it is strongly hindered. It may be supposed that there occurs in the $O{-}CH_2$ fragment a special interaction, consisting in partial overlapping between the orbitals of the C–H bonds and those of the lone pairs of electrons of the oxygen atom (*p*–σ conjugation):

$$\left[-O-CH_2 \leftrightarrow -O^+{=}C- \leftrightarrow -O^+{=}C-\right]$$

(H⁻ on the C–H bond; H on the C–H bond; H⁻ on the terminal CH₂)

2-Chloroethyl vinyl ether is obtained by the dehydrochlorination of bis-2-chloroethyl ether (Chlorex)[160–162], dioxan and small amounts of divinyl ether and acetaldehyde being formed as byproducts[163]. The production of 2-chloroethyl vinyl ether by the pyrolysis of 2-chloroethoxyethyl acetate has been reported[164]. The complete dehydrochlorination of Chlorex provides a convenient route for obtaining divinyl ether itself[165–167]. 2-Bromoethyl vinyl ether has been prepared from bis-2-boromethyl ether[168]. Examples are known of the preparation of an allyl vinyl ether via allyl 2-bromoethyl ether[169,170]. α-Substituted alkyl vinyl ethers have been prepared[171,172] by means of the scheme

$$CH_2{=}CHOR \xrightarrow{Br_2} CH_2BrCHBrOR \xrightarrow{R'MgX} CH_2BrCH(R')OR \xrightarrow[KOH]{-HBr} CH_2{=}C(R')OR\ (80\%).$$

Vinyl ethers of β-silicon-containing alcohols have been synthesised by dehydrochlorination[173]:

$$R_3SiH + CH_2{=}CHOCH_2CH_2Cl \rightarrow R_3SiCH_2CH_2OCH_2CH_2Cl \xrightarrow[350-400^\circ]{KOH} \rightarrow R_3SiCH_2CH_2OCH{=}CH_2\ (75\%).$$

The vinyl ether of glycidol has been prepared by dehydrochlorinating the corresponding 2-chloroethyl ether[174]:

$$ClCH_2CH_2OCH_2CH(O)CH_2 \xrightarrow[200^\circ]{NaOH} CH_2{=}CHOCH_2CH(O)CH_2.$$

Aryl 2-halogenoethyl ethers are considerably more easily dehydrohalogenated[72,153,175]. This can be explained in terms of the above considerations by the part played by the lone electron pairs of the oxygen atom in conjugation with the benzene ring, so that the effect of *p*–σ conjugation with the α-C–H bonds is weakened.

Certain fluorinated vinyl ethers can be synthesised as follows[176]:

$$CH_2(O)CH_2 + ROH \rightarrow HOCH_2CH_2OR \rightarrow ClCH_2CH_2OR \xrightarrow{-HCl} CH_2{=}CHOR,$$

where R = CH_2CHFCl, CH_2CF_3, $CH_2C_2F_5$, $CH_2C_3F_7$. Fluorinated alkenes have been used for the same purpose[177]:

$$HOCH_2CH_2OH + F_2C{=}CFCl \xrightarrow{Na} HOCH_2CH_2OCF_2CHFCl \xrightarrow[I_2]{P} \rightarrow ICH_2CH_2OCF_2CHFCl \xrightarrow[CaO]{NaOH} CH_2{=}CHOCF_2CHFCl.$$

The series of reactions

$$ROH + COF_2 \xrightarrow{100-120^\circ} ROCOF \xrightarrow{SF_4} ROCF_3 \xrightarrow[C_2H_5OH]{KOH} CH_2{=}CHOCF_3,$$

where R = $ClCH_2CH_2$, $BrCH_2CH_2$, has been proposed[178] for the preparation of trifluoromethyl vinyl ether. The same route has been used to synthesise[178] dichlorovinyl trifluoromethyl ether $CCl_2{:}CHOCF_3$ from trichloroethanol.

Divinyl ethers of *gem*-diols (divinyl acetals) have been obtained by dehydrochlorination of the corresponding 2-chloroethyl acetals[179–181]. Unsymmetrical alkyl 2-chloroethyl acetals have similarly been used[179,180] for the synthesis of α-alkoxylated vinyl ethers (alkyl vinyl acetals) $CH_3CH(OR)OCH{:}CH_2$. Formaldehyde alkyl 2-halogenoethyl acetals $ROCH_2OCH_2CH_2X$ (where X = Cl, Br) treated with potassium hydroxide at 350–400°C yield[182] alkoxymethyl vinyl ethers $CH_2{:}CHOCH_2OR$.

In the case of chloroacetaldehyde bis-2-chloroethyl acetal all three possible vinyl ethers can be isolated[183]. Elimination occurs with greatest difficulty in the aldehyde

part of the molecule, where, according to the ideas discussed above, the single β-hydrogen atom (relative to the halogen) under attack by bases is able to interact by means of its σ-bond with the *p*-electrons of the two oxygen atoms at once. As a consequence its proton mobility is considerably restricted.

Dehydrochlorination has been applied also to cyclic acetals of glycerol chlorohydrin[184]. Chloroacetaldehyde acetals of glycols, glycerol, glycerol chlorohydrin, diethylene glycol, pentaerythritol, mannitol, and sorbitol do not split off hydrogen chloride on treatment with caustic potash in butanol, but form the corresponding acetals of butoxyacetaldehyde[185]. Dehydrochlorination takes place only in the presence of potassium t-butoxide.

IV. VINYL EXCHANGE

Vinyl ethers[186-192] and esters[193-197] are able to exchange their vinyl groups with alcohols in the presence of mercury salts:

$$ROCH{=}CH_2 + R'OH \xrightarrow{Hg^{2+}} ROH + R'OCH{=}CH_2$$

where R = alkyl or acyl. The reaction makes it possible to obtain vinyl ethers containing functional groups which are unstable in the presence of bases. The catalyst is usually mercury acetate or sulphate, while the vinylating agent is an alkyl vinyl ether[186-191], phenyl vinyl ether[192], or vinyl acetate[193-195,197].

The mechanism of exchange is complicated and has not been finally elucidated. The concept of π-complexes explains activation of the vinyl ether, but not the actual act of vinyl migration. It appears paradoxical that a vinyl ether and an organic acid (or alcohol) can coexist in the presence of mercury salts, which are among the most active catalysts of electrophilic addition. It is probable that the hydroxy-component which is formed combines with excess of the vinylating agent to produce the corresponding acetal or acylal.

Vinyl exchange involving vinyl acetate has been explained[197] by dissociation to yield a mercury–acetylene complex and acetic acid:

$$CH_2{=}CHOCOCH_3 \overset{Hg^{2+}}{\rightleftharpoons} [C_2H_2 \cdot Hg^{2+}] + CH_3COOH.$$

According to Watanabe and Conlon[189], vinyl ethers first add the catalyst at the multiple bond:

$$Hg(OAc)_2 \rightleftarrows HgOAc^+ + AcO^-$$

$$HgOAc^+ + ROCH{=}CH_2 + R'OH \rightleftarrows \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + H^+$$

$$\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + ROCH{=}CH_2 + R'OH$$

$$\downarrow\uparrow$$

$$\left[\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2-\right]_2 Hg + HOAc$$

$$\downarrow\uparrow$$

$$\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + R'OCH{=}CH_2 + ROH$$

However, kinetic investigations using isotopes[198] indicate that vinyl exchange catalysed by mercury salts does not involve the intermediate formation of mercury–acetylene complexes or intermediate acetoxymercuration, and therefore a mechanism of direct substitution has been suggested[198].

Vinyl transetherification is widely used for the preparation of functional alkoxyethylenes. Vinyl ethers of several diols have been obtained[187,191,197]. The vinylation of the methyl ester of glycollic acid has been reported[197]. Various vinyl ethers have been used[189,190] for the vinylation of ethylcellulose, allyl, methylallyl, and chloroallyl alcohols, ethylene chlorohydrin, ethylene cyanohydrin, 2-nitropropanol, and 4-hydroxypentan-2-one. Boiling divinylcarbinol in excess of ethyl or isobutyl vinyl ether with mercury acetate and sodium acetate yields[199] the vinyl ether $(CH_2:CH)_2CHOCH:CH_2$. Phenyl vinyl ether has been successfully used[192] for vinylating 2-naphthol, *p*-phenylphenol, and quinol with mercury acetate as catalyst. American workers[200] have obtained the vinyl ethers of phenol, *p*-cresol, and 2,6-dichlorophenol in yields of 80–100%, using divinylmercury as vinylating agent. Polyfluorinated vinyl ethers have been synthesised[201] by the transetherification of vinyl acetate with fluorinated alcohols. The vinyl transetherification of the methyl and ethyl ethers of hydrobenzoin with butyl vinyl ether has been investigated[69,202]. When salicylic acid is treated with vinyl acetate in the presence of mercury acetate, only a cyclic acylal (2-methyl-4-oxobenzo-1,3-dioxan) can be isolated[203].

V. SYNTHESES OF VINYL ETHERS BASED ON THE REACTIONS OF FUNCTIONAL GROUPS IN SUBSTITUTED VINYL ETHERS

The chief obstacles in the way of accomplishing such reactions are the difficult accessibility of functional vinyl ethers capable of further modification involving the functional substituent and the great reactivity of the vinyloxy-group itself. Mild conditions are usually required, and *electrophilic* reagents are then usually unsuitable. Nevertheless, these methods possess great synthetic possibilities.

1. Monovinyl Ethers of Glycols

Until quite recently only a few isolated examples were known of the synthesis of functional ethers from monovinyl ethers of glycols[76,204-208]. After a technically practicable route had been found for synthesising 2-vinyloxyethanol at atmospheric pressure, in the course of the development and industrial exploitation of a mercury-free technology for producing acetaldehyde via vinyl ethers of glycols[21,91], the widespread use of this compound in organic synthesis actually became possible.

Researches carried out during recent years[209] have enabled certain general rules to be formulated for the selective modification of functional fragments of a vinyl ether, and have shown that hydroxylated vinyl ethers may become a new, readily available source of polyfunctional monomers.

New unsaturated diethers were obtained by treating the sodium derivatives of monovinyl ethers of glycols with prop-2-ynyl bromide[210,211]:

$$CH_2{=}CHORONa + BrCH_2C{\equiv}CH \rightarrow CH_2{=}CHOROCH_2C{\equiv}CH.$$

Vinyloxyalkoxyalkynols have been synthesised[212,213] by the reaction

$$CH_2{=}CHOROCH_2C{\equiv}CH + R'R''C{=}O \rightarrow CH_2{=}CHOROCH_2C{\equiv}CCR'R''OH.$$

This reaction has since been applied to other examples[214]. Dehydration of the products[213] yields vinyl ethers containing

an enyne bond system in the alkoxy-radical. Propynyloxyalkyl vinyl ethers react[215,216] with trimethylchlorosilane, both as its sodium and as its magnesium bromide derivative, to form trimethylsilylpropynyloxyalkyl vinyl ethers:

$$CH_2{=}CHOROCH_2C{\equiv}C\,(Na)\,MgBr + ClSi(CH_3)_3 \rightarrow CH_2{=}CHOROCH_2C{\equiv}CSi\,(CH_3)_3.$$

The corresponding reaction with triethyltin chloride yields triethylstannylpropynyloxyalkyl vinyl ethers[217]. Trialkylstannylalkynyl vinyl ethers are obtained by the reaction of alkynyl vinyl ethers containing a terminal acetylenic group with hexa-alkyldistannoxanes and trialkylstannyloxyalkanes[218].

The behaviour of propynyloxyalkyl vinyl ethers under the conditions of the Mannich condensation has been studied[219,220], and dialkylaminobutynyloxyalkyl vinyl ethers have been synthesised:

$$CH_2{=}CHOROCH_2C{\equiv}CH + CH_2O + HNR'_2 \rightarrow CH_2{=}CHOROCH_2C{\equiv}CCH_2NR'_2.$$

The same scheme has been since used[221] to synthesise the ether $CH_2:CHOCH_2CH_2C:CCH_2N(C_2H_5)_2$. Potassium t-butoxide in t-butyl alcohol converts propynyloxyalkyl vinyl ethers into the corresponding allenes[222] $CH_2:CHOROCH:C:CH_2$. Successive treatment of vinyloxyethyne with lithamide in liquid ammonia and with butyl bromide[158] converts it into 1-vinyloxyhexyne in 60% yield.

The cyanoethylation of monovinyl ethers of glycols is accompanied[223-225] by the formation of β-vinyloxyalkoxypropionitriles $CH_2:CHOROCH_2CH_2CN$. When these compounds are reduced with lithium tetrahydroaluminate[226], the expected aminoalkyl vinyl ethers are not formed, but the initial molecule undergoes almost quantitative cleavage at the carbon–oxygen bond in the cyanoethoxy-group:

$$CH_2{=}CHOROCH_2CH_2CN \xrightarrow{LiAlH_4} CH_2{=}CHOROH + CH_3CH_2CH_2NH_2.$$

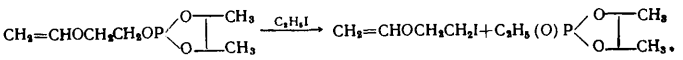
A similar cleavage is observed when the cyanoethoxyalkyl vinyl ethers react with sodium in alcohol[226]. An attempt has been made[227] to prepare the corresponding ketones from these ethers by the Grignard synthesis, but the main reaction products were vinyloxyalkanols and polymeric materials:

$$CH_2{=}CHOROCH_2CH_2CN + R'MgX \rightarrow CH_2{=}CHOROMgX + \text{polymer}.$$

Secondary amines together with paraformaldehyde smoothly aminomethylate monovinyl ethers of glycols, provided that the water evolved is removed azeotropically[225,228,229]. When dialkylaminomethoxyalkyl vinyl ethers interact with alcohols and with thiols[230], the expected addition of the reagents at the vinyl group is not observed, but the carbon–oxygen bond in the aminomethoxy-group undergoes cleavage with formation of the monovinyl ether of the glycol and the corresponding amine.

The monovinyl ethers of mono-, di-, and tri-ethylene glycols react with trimethylchlorosilane to give the corresponding silyl vinyl ethers of the glycols[225,231]. The sodium derivatives of hydroxylated vinyl ethers give with triethyltin chloride almost theoretical yields of triethylstannyloxyalkyl vinyl ethers[225,232,233]. Several vinyl ethers containing an ester group have been synthesised[234] by the interaction of acyl halides with vinyloxyalkanols in the presence of triethylamine. Chlorides of phosphorous acids form with monovinyl ethers of glycols[235,236] or their sulphur analogues[237] a new series of reactive trialkyl phosphites $(AlkO)_2POR$, where $R = CH_2:CHO[CH_2]_2$, $CH_2:CHO[CH_2]_2S[CH_2]_2O$, $CH_2:CHS[CH_2]_2$, etc.

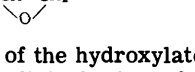
Arbuzov rearrangement of 4,5-dimethyl-2-vinyloxyethoxy-1,3,2-dioxaphospholan in the presence of ethyl iodide yields 2-iodoethyl vinyl ether[238]:



A quantitative yield of dialkyl vinyloxyalkyl phosphorothionates has been obtained[239] by the reaction

$$CH_2{=}CHOCH_2CH_2OP(OC_2H_5)_2 \xrightarrow{S} CH_2{=}CHOCH_2CH_2O(S)P(OC_2H_5)_2.$$

A detailed investigation has been made[240] of the reaction of monovinyl ethers of glycols with epichlorohydrin, and a series of glycidyloxyalkyl vinyl ethers



have been synthesised. Excess of the hydroxylated component favours the formation of a divinyl ether of the structure

$$CH_2{=}CHOROCH_2CH(OH)CH_2OROCH{=}CH_2$$

by a secondary reaction involving the glycidyl fragment. Subsequent cleavage of the oxide ring by means of thiols, amines, metal derivatives of acetylenes, and organochlorosilanes provides a ready method for obtaining the corresponding substituted vinyl ethers[241,242].

2. Halogenated Vinyl Ethers

Halogenoalkyl vinyl ethers possess no less potentialities for the synthesis of functionally substituted alkoxyethylenes, although 2-chloroethyl vinyl ether still remains the only one which is available. Before the start of systematic investigations on vinyl ethers of halogenated alcohols[243,244] there were a few examples of the use of 2-chloroethyl vinyl ether for the preparation of vinyl ethers containing functional substituents (the reactions with alkoxides[245], benzonitrile[246], *N*-substituted 2-trifluoromethylphenothiazines[247], and trialkyl phosphites[248]). It would be of great interest for organic synthesis to obtain a Grignard reagent from halogenoalkyl vinyl ethers. However, the only known attempt in this direction[168], based on 2-bromoethyl vinyl ether, was unsuccessful, this ether being found to decompose into acetylene and ethylene on treatment with magnesium. Similar breakdown was observed[168] on interaction with metallic sodium.

Investigations of nucleophilic substitution of the chlorine atom in 2-chloroethyl vinyl ether[244] have confirmed that, in alcoholic solutions of alkoxides, the latter forms around 30% yields of 2-alkoxyethyl or 2-aryloxyethyl vinyl ethers. The course of the reaction is similar in liquid ammonia with but-3-ynol[249], obtained directly in the reaction medium from ethylene oxide and sodium acetylide. Alk-1-ynes, in the form of their sodium derivatives, are alkylated by 2-chloroethyl vinyl ether in liquid ammonia[250], but the rate of the reaction is fairly low. Replacement by an alkylthio- or arylthio-group takes place considerably more easily[244,251], and treatment with sodium sulphide yields the divinyl ether of thiodiglycol[244]. The reaction of 2-chloroethyl vinyl ether with secondary amines has been used[252] as a basis for a convenient method of synthesising 2-dialkyl(aryl)aminoethyl vinyl ethers of diverse structure. Treatment of 2-chloroethyl vinyl ether with sodium iodide in acetone resulted in replacement of the chlorine atom by iodine[244]. 2-Iodoethyl vinyl ether alkylates tertiary

amines with formation of the corresponding vinyloxyethyltrialkylammonium salts[244], and on treatment with potassium fluoride in diethylene glycol[253] is converted into 2-fluoroethyl vinyl ether. It has been proposed[254] to use vinyl ethers of halogenated phenols for the synthesis of aryl vinyl ethers containing alkyl and alkoxyl groups.

3. Nitrogen-containing Vinyl Ethers

Use of the divinyl ether of bishydroxyethylamine for the aminomethylation of acetylene[255], alcohols[255,256], and thiols[256] opens up a simple path to various classes of nitrogen compounds containing a vinyloxy-group—$R_2C{:}CH$, $RC{:}CR$, $RC{:}CCH_2OH$, $RSCH_2CH{:}CH_2$, etc., where R = $CH_2N(CH_2CH_2OCH{:}CH_2)_2$.

On treatment with vinyl acetate the vinyl ether of aminoethanol and the divinyl ether of bishydroxyethylamine form[257] the corresponding *N*-acetyl derivatives. With methyl chloroacetate the divinyl ether of bishydroxyethylamine gives methyl *NN*-bisvinyloxyethylaminoacetate $(CH_2{:}CHOCH_2CH_2)_2NCH_2COOCH_3$.[258] Methyl *β-NN*-bisvinyloxyethylaminopropionate[258] has been prepared from the divinyl ether of bishydroxyethylamine and methyl acrylate:

$$(CH_2{=}CHOCH_2CH_2)_2NH + CH_2{=}CHCOOCH_3 \xrightarrow{100^\circ} \rightarrow (CH_2{=}CHOCH_2CH_2)_2NCH_2CH_2COOCH_3 .$$

The addition of the vinyl ether of aminoethanol to methyl methacrylate has also been reported[259].

In the course of a study of the cycloaddition of dialkylketens to vinyl ethers[260] it was noted that initially the vinyl ether of aminoethanol undergoes vigorous acylation at the amino-group.

Vinyloxyalkylcyanamides[261,262] are formed by reaction between aminoalkyl vinyl ethers and a cyanogen halide:

$$CH_2{=}CHOCH_2CH_2N(R)H + NCHal \rightarrow CH_2{=}CHOCH_2CH_2N(R)CN,$$

where R represents methyl, allyl, or cyclohexyl. The resulting ethers react with dicyandiamide to form[262] *N*-methyl-*N'*-vinyloxyethylmelamines. Treatment of aminoalkyl vinyl ethers with potassium cyanate[263] in acidified water (pH > 6.8) yields vinyl ethers of hydroxyalkylated ureas. Analogous compounds have been synthesised by reaction between urea and aminoalkyl vinyl ethers. Treatment of isocyanatoalkyl vinyl ethers with aqueous ammonia and with aziridine[264,265] also yields the corresponding vinyl ethers containing a ureido-group:

$$CH_2{=}CHOCH(CH_3)CH(CH_3)N{=}C{=}O \xrightarrow[HN]{NH_3} \begin{cases} \rightarrow CH_2{=}CHOCH(CH_3)CH(CH_3)NHCONH_2 \\ \rightarrow CH_2{=}CHOCH(CH_3)CH(CH_3)NHCON \end{cases}$$

Acylation of aminophenyl vinyl ethers with acid chlorides has been used[266] to synthesise vinyloxyanilides of various acids, as well as bis-*p*-vinyloxyphenylurea and isopropyl *m*- and *p*-vinyloxyphenylcarbamates. Reaction between ammonium dialkyl phosphorodithioates and *p*-chloroacetamidophenyl vinyl ether yields[266] *OO'*-diethyl *S*-*p*-vinyloxyphenylcarbamoylmethyl phosphorothiolothionate $p\text{-}CH_2{:}CHOC_6H_4NHCOCH_2SPS(OC_2H_5)_2$.

The acylation of vinyl ethers of aminophenols by means of anhydrides of organic acids have also been described[135,267]. Interation of vinyl ethers of aminophenols with acrylaldehyde and with furfuraldehyde forms the basis of proposed methods for the preparation of vinyl ethers of alkenyl- and furyl-aldiminophenols[268,269].

Whereas dialkyl phosphorodithioates add readily at the double bond in aryl vinyl ethers containing no substituents of basic character in the ring[266,270], aminophenyl vinyl ethers form salts $[CH_2{:}CHOC_6H_4NH_3]^+[(RO)_2PSS]^-$ in the analogous reaction[271]. Reduction of vinyl ethers of nitrophenols in alkaline medium yields divinyl ethers of azo- and azoxy-phenols[272,273].

4. Divinyl Ethers

The addition of hydrogen chloride to divinyl ether itself takes place in stages, and ultimately 1-chloroethyl vinyl ether can be isolated in yields up to 60%.[158,165] When divinyl ether interacts with carbon tetrachloride[274] it is difficult to retard the reaction in any way substantially at the first stage, the yield of tetrachloropropyl vinyl ether being only 17%. Divinyl ether undergoes the Diels–Alder reaction with hexachlorocyclopentadiene[275,276] and with anthracene[277]. Two adducts are formed, the yields of which depend on the proportions of the components and the temperature of the reaction. Some divinyl ethers of glycols have been subjected to hydroxylation[278,279], but monoadducts have not been isolated.

Hemiacetals (1-hydroxyalkyl vinyl ethers) $RCH(OH)OCH{:}CH_2$ have been obtained[280] by interaction between divinylpropanals and mercuric oxide in the presence of mercury acetate in aqueous–alcoholic medium.

Promising routes for the synthesis of functionally substituted vinyl ethers from divinyl ethers will probably be opened up by the investigation of reactions of homolytic addition occurring preferentially at one of the vinyloxy-groups.

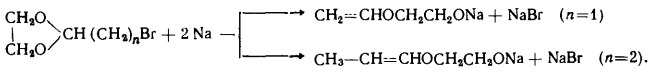
VI. CATALYTIC ELIMINATION IN A SERIES OF FUNCTIONAL ACETALS

The preparation of vinyl ethers containing functional substituents by eliminating one alcohol molecule from an appropriate acetal has not yet become widely used. The initial functional acetals are in general difficultly accessible compounds, being in several cases most easily obtained actually from vinyl ethers. Another reason lies in the conditions of the reaction[281–285], which are often either severe or altogether inapplicable with certain functional groups. The method is used mainly for the preparation of 2-substituted vinyl ethers[283,286–288] of the type $AlkCH{:}CHOAlk$ which cannot be obtained by direct vinylation. Nevertheless, the literature contains several examples of the use of this method for obtaining vinyl ethers of functional alcohols (allyl vinyl ether[289,290], ethyl vinyl ether of ethylene glycol[282], a polyfluorinated vinyl ether $CH_2{:}CHOCH_2CF_3$,[291,292] alkynyl vinyl ethers[293,294]). When unsymmetrical alkynyl ethyl acetals undergo cleavage[214], the relative proportions of ethyl vinyl and alkynyl vinyl ethers depend on the structure of the radical, the yield of acetylenic ether increasing in the sequence $CH_2C{:}CH$ (5%) < $CH_2CH_2C{:}CH$ < $CH(CH_3)CH_2C{:}CH$ (70%). From this we conclude that the acid-catalysed pyrolysis of unsymmetrical acetals takes place predominantly with elimination of the most electronegative radical and formation of the more stable carbonium ion $[CH_3CHOR]^+$.

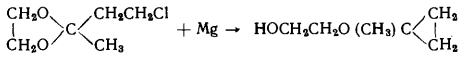
VII. OTHER METHODS

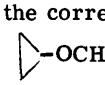
1. Interaction of Acetals of α-Halogenoaldehydes with Metals

This method[295] is seldom used in practice, and then mainly for the preparation merely of vinyl ethers of monohydric alcohols[286,296,297]. Among functional vinyl ethers it is probable that only hydroxylated αβ-unsaturated ethers are obtained in this way[76,298,299]:



Feugeas and Normant[300] reported that the action of metallic magnesium in ether on the cyclic acetal of α-chloroacetone (2-chloromethyl-2-methyl-1,3-dioxolan) gave not an organomagnesium compound but the 1-methylvinyl monoether of ethylene glycol. The same reaction with cyclic acetals of β-halogeno-ketones yields not a vinyl ether but an ether of cyclopropanol:



Cyclic acetals of αγδξ-halogeno-ketones react similarly with metallic magnesium, forming 2-hydroxyethyl ethers of the corresponding cyclic alcohols. Apparently Hill and Pidgeon[298] were dealing not with 2-methyl- and 2-ethylvinyl ethers of ethylene glycol but with the corresponding cyclopropanol derivatives ,  .

2. Reaction of Alkoxides of Functional Alcohols with Vinyl Halides

The possibility of extending the Butlerov reaction[301] to functional alcohols has been demonstrated by the synthesis of vinyl ethers of ethylene glycol by heating (to 80–90°C) vinyl chloride with sodium glycolates under pressure[302]. It is not excluded that the process may be only formally a case of nucleophilic substitution, the reaction actually involving an intermediate stage in which free acetylene is formed[6].

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Synthesis of Ion-exchange Membranes

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Extensive research has been conducted during recent years on the synthesis, properties, and applications of ion-exchange membranes. On the basis of the periodical and patent literature the paper gives a systematic account of membranes and methods for their production, the various ways of synthesising them, and brief information on their application and the laws of membrane processes. Classification is based on various criteria, primarily the homogeneity, the nature of the skeleton and the character of functional groups, electrochemical properties, etc.
Numerous methods of synthesising and producing polymerisation and polycondensation membranes, activated films, and heterogeneous membranes are described and critically examined. The main reactions are given. From an analysis of the literature, patents, and other sources the prospects are given for possible future developments in the synthesis of ion-exchange membranes. A list of 367 references is included.

CONTENTS

I. Introduction 920
II. Classification of membranes 920
III. Properties of ion-exchange membranes 922
IV. Methods of synthesising ion-exchange membranes 922
1. Heterogeneous membranes 922
2. Homogeneous membranes 922
3. Interpolymer membranes 927

I. INTRODUCTION

Ion-exchange polymers are used in many fields of science and technology. Depending on the character of the process, the exchangers are employed in the form of particles varying in geometrical shape and size. They are most widely used as granules and sheets (membranes). Methods for the synthesis of ion-exchange resins of the former type are well known and have been widely described [1,2]. Methods which have hitherto been proposed for the synthesis of ion-exchange membranes have been reported almost exclusively in the patent literature and in a few review papers [3-14], which contain a brief list of processes for obtaining membranes, published over a definite period of time.

The first specimens of membranes (heterogeneous), based on industrial exchangers, were obtained in 1950 by Wyllie and Patnode [15]. The synthesis of homogeneous membranes was first described by Manecke [16] and by Sollner and Neihof [17] in 1951, and later Gregor and his co-workers [18,19] synthesised interpolymer membranes.

With expansion in the possible fields of application of membrane processes, the demands made on membranes have risen, and consequently new types of membranes and methods for synthesising them have appeared.

The applications of ion-exchange membranes show great variety. Particularly important uses are the desalination of salt-water and of brackish waters, the preparation of high-purity metals, and recently the production of fuel cells. Membrane methods of desalination—electrodialysis [20-31,33,34], ion-osmosis [32], and hyperfiltration [35-37]—have aroused great interest. Promising uses of ion-exchange membranes are the preparation of pure metals, the isolation of certain metals from their mixtures with others, the separation of elements of closely similar properties, etc. [26,38-45].

Fuel cells provide a new field for the application of ion-exchange membranes [46-52], whose use has such advantages as decreasing the weight of the fuel cells, the absence of a liquid electrolyte, and the possibility of obtaining pure water when hydrogen and oxygen are employed. The prospects for the use of membrane processes are very promising.

II. CLASSIFICATION OF MEMBRANES

The literature on ion exchange contains no papers specially devoted to the classification of membranes. This question is sometimes touched on in review papers and monographs. Laskorin et al. [45], Morgan [53], Lyubman and Shostak [14], and Hasenberg [54] discuss ion-exchange membranes mainly from the point of view of structure. There is as yet no rigorous scientific classification of membranes and methods of synthesis, based on a single common criterion. It is difficult to make such a classification.

An attempt is made in the present paper to give a practical classification, based on various criteria, of the membranes which have been described in the periodical and the patent literature. A distinction must be made between films and ion-exchange membranes: films consist of inert, uncharged polymers, whereas ion-exchange membranes are insoluble polyelectrolytes, containing positively or negatively charged groups, in the form of sheets, plates, discs, rods, etc. The term "diaphragms" is applied in most cases to inorganic membranes [55-57].

Ion-exchange membranes are of either natural or synthetic origin. Each type is divided according to its chemical character into organic and inorganic [55-65]. Examples of organic natural membranes are proteins, the skin of frogs, and ox bladder; while inorganic natural membranes include insoluble minerals containing calcium, several zeolites, and clays.

Depending on their type of selectivity, membranes are either (1) permeable to ions having charges of one sign and impermeable to oppositely charged ions and water, or (2) permeable to water but impermeable to ions. The former type are used in electrodialysis, mainly for demineralising water [66-77] and separating metals [38-40,78-83]; while the latter are still in the research stage, and may find application predominantly in hyperfiltration processes for the demineralisation of water [35,84-121].

Membranes are divided into ionogenic, complexing, and redox membranes according to the character of the fixed groups. Ion-exchange membranes contain acidic or basic functional groups. In complex-forming membranes the functional groups are able to form complexes with various

elements[122-126]. Such membranes have been obtained, for example, from a copolymer of di-isobutyl vinylphosphonate and acrylic acid[122], the resin Dowex A-1 and poly(vinyl chloride)[124], etc. These membranes have not yet found sufficiently wide application. Redox membranes contain oxidation–reduction groups instead of ionogenic groups.

According to the acid–base function of the ionogenic groups we can distinguish cation-exchange, anion-exchange, and amphoteric membranes. Cation-exchange membranes containing the strongly dissociated sulpho-group are said to be strongly acidic[127-169], while groups of moderate or low degree of dissociation (phosphoric, carboxylic) are said to be weakly acidic[170-173]. On this criterion anion-exchange membranes are in turn divided into strongly basic, containing the strongly dissociated pyridinium, quaternary ammonium, or rarely phosphonium or sulphonium groups[174-190], and weakly basic, having tertiary, secondary, or primary nitrogen atoms[191-199]. Amphoteric membranes contain both negatively charged and positively charged ionogenic groups[200-203]. These membranes play an important part in the vital activity of living cells. They are mostly membranes of animal (mainly proteins) or vegetable (mainly lignin) origin. Depending on the pH of the surrounding medium, protein membranes function as inert at a hydrogen-ion concentration corresponding to the isoelectric point, as anion exchangers at lower pH values, and as cation-exchange membranes at higher pH. It has been proposed to synthesise amphoteric membranes, containing quaternary ammonium and carboxyl groups, by the copolymerisation of a homogeneous solution of a 5-ethyl-1-methyl-2-vinylpyridinium salt, methacrylic acid, styrene, and divinylbenzene in the presence of a plasticiser[201]. In another case a copolymer of methacrylic acid and 2-diethylaminoethyl methacrylate is used as the active component[200]. The main theoretical principles of membrane processes, worked out by Meyer and Sievers[204] and by others (see below) extend also to membranes of this type.

Depending on their structure, membranes are subdivided into heterogeneous, homogeneous, interpolymer, isoporous (synthesised by the Reviewers), bipolar, mosaic, and coated with an inert polymer film.

Heterogeneous membranes are two-phase systems, the ion-exchange resin being distributed in an inert binder[159-164,205-223]. Since a continuous phase of the ion-exchange component is not present in this case, transport of ions takes place as a consequence of contact between the resin particles or through solution present between them, the process often being governed by both factors.

Homogeneous membranes consist solely of the ion-exchange component, forming one continuous phase[127-154,224-298]. In most cases they are transparent and uniform for visible wavelengths ($\sim$ 4000 Å). Homogeneous membranes are now finding preferential dissemination in connection with their successful use in electrodialysis. According to their mode of production these membranes can be divided into condensation[133-139] and polymerisation[228-238] membranes, together with those based on inert polymer films[240-298]. This last group are divided in turn into sheet[141,142], graft[240-274], and film[275-298] membranes.

Interpolymer membranes, obtained by the molecular blending of two polymers, are similar in properties and structure to homogeneous membranes[74,76,299-338]. In membranes of this type molecular chains of the two components are closely interlinked, and the polyelectrolyte forms one phase, although chemical bonds are not usually present between the two polymers. This has a good effect on the properties of the membranes, in particular their mechanical stability, since on swelling in water no great stresses are produced in the membrane, owing to the mobility of one polymer molecule relative to another. Two types of interpolymer membranes—dynel[299-305] and those based on inert polymer films[306-315,330-336]—can be distinguished.

Membranes exist in which one surface is a cation exchanger, while the other is an anion exchanger. These are bipolar membranes[339-343]. Their most important feature is their selectivity towards hydrogen. A Japanese patent[343] proposes the synthesis of a bipolar membrane from a polyethylene film, styrene, and 4-vinylpyridine by the use of γ-radiation. A bipolar membrane can be obtained by sticking together sheets of cation-exchange and anion-exchange membranes prepared from the appropriate resins and a solution of poly(vinyl chloride) in cyclohexanol by a method of pouring[342]. The use of bipolar membranes has not become widespread.

Little is known about mosaic membranes[292,344]. They consist of sharply divided regions, one of which is permeable to cations, while the other is permeable to anions. A synthesis of mosaic membranes has been described[292]: polyethylene film is treated with sulphuryl chloride or a mixture of sulphur dioxide and chlorine, after which individual portions are treated with tetraethylenepenta-amine.

According to the state of aggregation membranes are divided into ordinary and liquid[345,346], and according to their physical structure into porous[347,348] and those having limited swelling (gel membranes). A further distinction is made between reinforced and unreinforced membranes. The reinforcement—unilateral, bilateral, or between the sheets—confers great mechanical strength on the membranes, but at the same time lowers their exchange capacity and their electrochemical parameters, while considerably increasing the cost[349].

Reference is made in the literature to the possibility of using as reinforcing material glass fibres[79,129,138], Saran[136,137,192], Teviron[299], and Vinyon[136] fabrics, nylon[163], capron[186], poly(vinyl chloride) and poly(vinylidene chloride) fibres[175], polyacrylonitrile[163,181,206], linear polyesters and polyamides[163,206], paper[208], etc. Glass cloth, poly(vinyl chloride), and other rigid materials are less suitable as reinforcements owing to their hydrophobic character and differences in the variation in their linear dimensions compared with the membrane material on contact with polar solvents and water. Use of an unsuitable reinforcing cloth encourages the appearance of microcracks and other chemical defects as a result of differences in the coefficients of expansion and also internal stresses. Investigations on the effects of reinforcements on the electrochemical properties of heterogeneous membranes of Ankalit A-7, synthesised from the anion-exchange resin AT-1 and low-density polyethylene, have established[349] that bilateral reinforcement greatly increases the mechanical strength and permits the amount of the ion-exchange component to be increased at the expense of the binder; the electrical conductivity of the membrane is almost doubled. Capron, Saran, and Vinyon provide the most suitable reinforcement for this type of membranes. The improved adhesion of the resin to such fibres is explained by the presence of identical groups (e.g. amino) in the two structures.

Membranes can be distinguished from one another also by the location of the functional groups: an ionogenic group may be situated in the main chain[66,67,128,130] or in a side-chain[193] of the polymer.

Finally, the ion-exchange membranes can be subdivided according to the nature of the starting material, which may be a monomer[69,72], a monomer containing an

ionogenic group[131,145], a polymer containing an ionogenic group[159-164,205-223] or none[229,230], a copolymer[130,228], or various polymer films[287-298].

Neither in the Soviet nor in the foreign literature does there exist a unified chemical terminology for membranes, and arbitrary names, given by individual authors or firms, have become widely used. In the USA, for example, Amberplex, Nepton, Permutit, Nalfilm, Amfion, Jonac, etc. brands of membranes are marketed; in England, Permaplex, Zerolit, etc.; in Japan, Selemion, Scrion, Neozeplan, Neozepta, etc.; and in the USSR, MK-40, MA-40, MA-41, MK-100, MA-100 Ankalit, etc.

III. PROPERTIES OF ION-EXCHANGE MEMBRANES

An ideal ion-selectively permeable membrane allows ions of only one sign to pass through on application of an electric potential gradient, independently of the concentration of the external solution. Ion-selective permeability should be combined with high electrical conductivity, mechanical strength, elasticity, and thermal and chemical stability. Some of these properties are completely incompatible, and therefore ideal membranes cannot be obtained. The electrochemical properties of membranes are independent of their geometrical shape: membrane potentials, among the most important of properties, are identical for discs, rods, and strips provided that these are of the same composition[350].

The founders of the theory of selectively permeable membranes and their electrochemical properties were Teorell[351] and Meyer and Sievers[204]. According to this theory the selective permeability of ion-exchange membranes can be explained by the presence of mobile charged ions and counter ions in the membrane phase.

A considerable contribution to the study of the electrochemical properties of ion-exchange membranes has been made by Soviet scientists. The theoretical foundations of the process of electrodialysis were established by I.I. Zhukov[352], and his pupils Laskorin, Smirnova[353,354], Nikol'skii, Materova, Stefanova[355], Belinskaya[218], and others have made detailed investigations of the properties of various ion-exchange membranes. Some of the results of these investigations have been used in the book by Laskorin et al.[45].

IV. METHODS OF SYNTHESISING ION-EXCHANGE MEMBRANES

1. HETEROGENEOUS MEMBRANES

All the methods which have been proposed for producing heterogeneous membranes are based on combining a finely divided ion-exchange resin with an inert binder and then forming the mass into a film. These methods are distinguished by the technology of preparation, the state of aggregation of the binder, or its chemical nature. The properties of the membranes depend in considerable measure on the quantity and the degree of subdivision of the initial exchanger. The content of active component in the membrane usually varies over the range 60–80%. Increase in its content is accompanied by a considerable decrease in mechanical strength as well as the increases in electrical conductivity and in exchange capacity of the membrane. The proportions of ion-exchange resin and of binder must therefore by selected so that the membrane does not deform or disintegrate during use.

A fraction of particle size not exceeding 100 μm is usually taken. Thermoplastic substances—polyethylene, polystyrene, poly(vinyl chloride), phenolic resins, polymethacrylic ester, synthetic and natural rubber, etc.—are especially widely used as binders. Inert materials are employed in the form of granules, powder, film, viscous mass, or solution.

A heterogeneous membrane can be obtained from practically any ion-exchange resin. It has been proposed[214,356] to compress the finely divided exchanger into sheets, which are then impregnated with a monomeric liquid, the latter being polymerised on further treatment.

In some cases the ion-exchange resin is introduced into the semi-liquid binder. Such a state is achieved either by adding a plasticiser or by keeping at an elevated temperature. After careful stirring the viscous mass is passed between rollers or pressed into sheets. If a plasticiser has been used, it is usually removed[75,187,215]. Membranes of this type possess improved mechanical strength. However, the use of high temperatures in the process of synthesis often impairs the properties of the exchangers, and it is therefore best to mix the resin and the binder at lower temperatures. A rubber latex can conveniently be used as the inert component[210,213].

A very interesting and effective way of modifying and improving heterogeneous membranes has been suggested by Laskorin et al.[222,357], who use a method of cross-linking with surface-active substances. Introduction of the latter enables a stable bond to be produced between the poorly compatible hydrophilic ion-exchange resin and the hydrophobic polymeric binder, with consequent decrease in the electrical resistance and increase in mechanical strength. The absence of reinforcement in cross-linked heterogeneous membranes considerably lowers their cost, and hence the cost of the demineralised water.

The following bands of heterogeneous ion-exchange membranes—Amberplex C-1 and A-1 (USA), Permaplex C-10, C-20, A-10, and A-20, Zerolit C-20 and A-20 (England), MK-40, MA-40 (USSR), etc.—are widely known at the present time.

Heterogeneous membranes possess several important defects—low electrical conductivity, high permeability to water, low resistance to the diffusion of electrolyte, and the possible formation of deposits inside the membrane—their high mechanical strength being due to reinforcement.

2. HOMOGENEOUS MEMBRANES

Because of the unsatisfactory electrochemical properties of heterogeneous membranes, extensive research has been undertaken during recent years on the synthesis of homogeneous membranes. The foundations of their synthesis are the reactions of polycondensation, polymerisation, and the chemical activation of inert films.

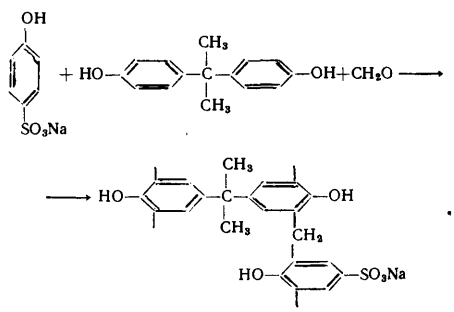
(*a*) Polycondensation Membranes

The starting materials most often used for this type of membranes are monohydric or polyhydric phenols, aromatic and aliphatic amines, urea and its derivatives, certain hydrocarbons, and other products. Choice of monomer is guided primarily by its chemical structure: the more reactive groups the initial compound contains the higher usually are the chemical stability of the final product and the three-dimensional interlocking of the individual chain units[358].

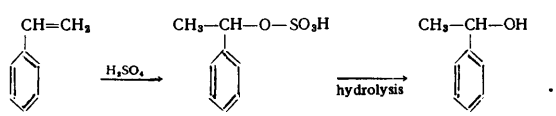
Ways of synthesising polycondensation membranes differ according to the medium in which the reaction is conducted, the nature of the initial monomers, and the process conditions. The first membranes were obtained from acidic aqueous mixtures containing hydroxybenzenesulphonic acid, melamine, or other similar monomer, formaldehyde, and a catalyst. It has been proposed to conduct polycondensation in an organic medium, e.g. methanol [138]. Morgan [53] refers to the production of polycondensation membranes by pouring the solutions on to the surface of mercury in a closed vessel. The more uniform and improved structure of the product is explained by the high thermal conductivity of mercury preventing the occurrence of local overheating.

Methods for the synthesis of polycondensation membranes have been most widely developed on the basis of hydroxybenzenesulphonic acid and formaldehyde [128,147]. The reaction can be conducted either in acid or in alkaline medium. The hydroxybenzenesulphonic acid can be replaced by the viscous product of the initial condensation of phenol with formaldehyde in the presence of acid or alkaline catalysts, followed by sulphonation of the resulting polymer [129]. In neither case do the membranes obtained possess adequate mechanical strength.

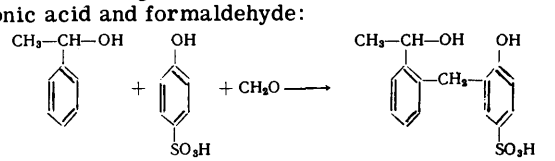
Improved membranes are obtained by condensing sodium hydroxybenzenesulphonate with phenol and formaldehyde [133,154]. Replacement of phenol by 2,2-diphenylpropane-*pp'*-diol yields specimens of enhanced stability, e.g. in solutions containing oxidising agents at 40°C [227]. The increased stability of the polymer is probably explained by the chemical nature of tne diol:



An interesting method has been suggested by Japanese chemists [143]. They took a mixture of phenol, styrene, and 98% sulphuric acid, preheated at 100–110°C, for cocondensation with formaldehyde and paraformaldehyde. Under these conditions sulphuric acid adds to the styrene at the vinyl bond, and the resulting partial sulphuric ester is hydrolysed:



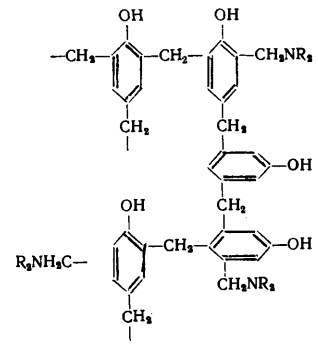
The product undergoes cocondensation with hydroxybenzenesulphonic acid and formaldehyde:



The use of styrene in the synthesis of polycondensation membranes apparently enables stronger specimens to be obtained, possessing diminished electrical resistance (in the present case 4 ohms cm^{-2}).

It has been proposed [153] to synthesise anion-exchange membranes by the polycondensation of tetraethylenepentaamine, ammonium sulphate, phenol, and formaldehyde in the presence of sulphuric and acetic acids. Replacement of the penta-amine by *o*-dimethylaminomethylphenol confers greater chemical resistance on the membrane, e.g. to the action of oxidants [193].

Japanese authors [198] suggest an original process for the industrial manufacture of anion-exchange membranes having a long service life. They use a resin in which the nitrogen atom constituting the central atom of the exchange base is not involved in the network structure of the resin:



For this purpose a compound of phenolic type containing a tertiary amino-group (e.g. $HOC_6H_4CH_2NR_2$) or a quaternary ammonium group is condensed with phenol and formaldehyde. The viscous resol resin is then formed into a film, and the gel ripened by heating. A membrane of this type is probably less suitable for use in electrodialysis, owing to its polyfunctionality.

Because of poor stability and low selectivity, especially in relatively concentrated solutions of electrolytes, polycondensation membranes have limited application.

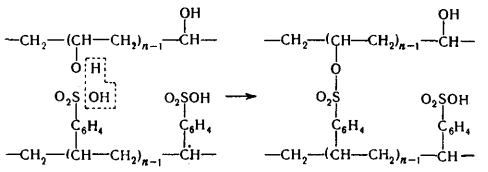
(*b*) Polymerisation Membranes

Membranes of this type are synthesised by the polymerisation or copolymerisation of unsaturated compounds, one of which should contain an ionogenic group or a group capable of transformation into such. Compounds containing vinyl groups are used, among them the aromatic compounds styrene, styrenesulphonic acid, and vinylpyridine, and the aliphatic vinylsulphonic, acrylic, and methacrylic acids, as well as salts, esters, and other derivatives of these compounds. The bridge-forming agents used are polyfunctional vinyl compounds—di- and tri-vinylbenzene, ethylene dimethacrylate, allyl acrylate, bismethylallyl ether, and other dienes and polyenes.

The above monomers are known to exhibit differing tendencies to polymerise, this constituting the main factor determining choice of the initial monomer in the synthesis. For example, cation-exchange membranes could have been more conveniently synthesised from styrenesulphonic acid, since sulphonation goes more easily with monomeric than with polymeric styrene; furthermore, polystyrene films on treatment with sulphonating agents undergo partial loss of their mechanical strength, and are deformed. But since styrenesulphonic acid is difficult to polymerise, in most cases polymerisation or copolymerisation of monomeric styrene with subsequent sulphonation is used.

Membranes possessing satisfactory electrical conductivity together with high mechanical strength are obtained from styrene and vinylsulphonic acid [145,152,182].

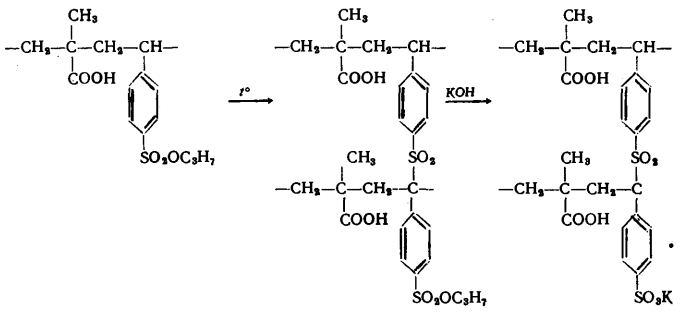
Synthesis is sometimes accomplished by using together styrene and styrenesulphonic acid [72] or styrenesulphonic acid with poly(vinyl alcohol) [134,232]. It has been suggested [314] that the combination of poly(vinyl alcohol) with poly(styrenesulphonic acid) occurs in conformity with the equation



To avoid the aqueous solubility of such a membrane and to ensure good electrochemical properties, the synthesis has been suggested of poly(styrenesulphonic acid) having a maximum content of sulpho-groups. An increase in the content of the acid in the copolymer from 20% to 60% is accompanied by an increase in the exchange capacity of the membrane from 1.1 to 2.8 mg-equiv. g^{-1}, while the electrical resistivity is halved. Even in the best specimens, however, the latter exceeds 500 ohm cm.

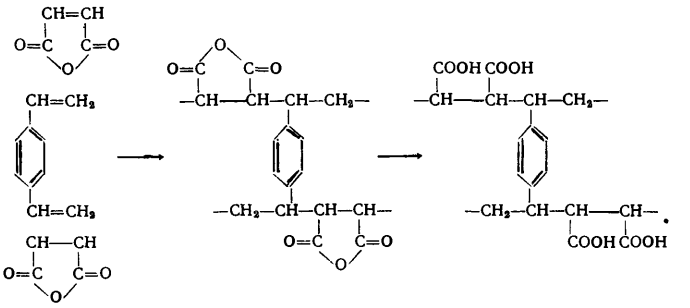
More promising is the use of styrenesulphonic esters mixed with other monomers. These esters polymerise more easily than does the acid itself, and are better combined with vinyl monomers (styrene, divinylbenzene, vinyl acetate, etc.).

Trostyanskaya et al. [131] synthesised cation-exchange membranes by the copolymerisation on various fabrics of toluene-*p*-sulphonic ester and divinylbenzene with subsequent sulphonation. The membranes possessed a high electrical resistance [131]. Sigodina et al. [66] obtained a cation-exchange membrane of low electrical resistance, but of poor mechanical strength, on the basis of copolymers of propyl styrenesulphonate and vinyl acetate. These workers [66] suggested the preparation of polyfunctional membranes based on copolymers of propyl styrenesulphonate and methacrylic acid, the membrane being vulcanised at 100°C for 5 h and then saponified. The process can be represented by the scheme



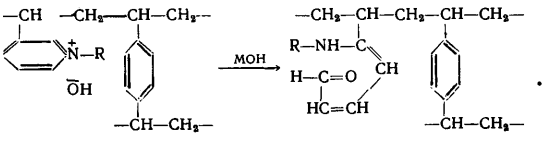
These membranes have greater mechanical strength than have monofunctional membranes. However, such membranes can hardly be used in electrodialytic desalination apparatus.

A carboxylated membrane of capacity 2.1 mg-equiv. g^{-1} has been synthesised by the copolymerisation of maleic anhydride with divinylbenzene in the presence of azoisobutyronitrile [231]. The reaction is conducted on the reinforcing fabric between two glass plates, the anhydride group then being hydrolysed [231]:



A Dutch patent [230] proposes the use of a complicated mixture—(1) a monomer (styrene, methacrylic or acrylic acid, methyl methacrylate), (2) its polymer, (3) a cross-linking agent (divinylbenzene or a mixture thereof with butadiene), and (4) a plasticiser not involved in the reaction—as starting materials for the synthesis of strongly and weakly acidic cation-exchange and anion-exchange membranes. Polymerisation is conducted in two stages, with partial (~25%) conversion of the monomer, addition of the remaining components, and completion of polymerisation. Ionogenic groups are introduced in the usual way. The final membranes are claimed to possess increased mechanical strength. Such membranes probably constitute a variety of ion exchangers of isoporous structure; the improved mechanical strength may therefore be assumed to be due to a more ordered polymer structure.

It has been proposed to synthesise most anion-exchange polymerisation membranes from vinylpyridine or its derivatives mixed with other components—polyepoxide compounds [78], quinol, styrene, butadiene [180], etc.—the vinyl-pyridine being alkylated during the synthesis with the formation of a pyridinium base. Membranes based on pyridinium compounds possess strongly basic properties, and are unstable in alkaline media [359]:

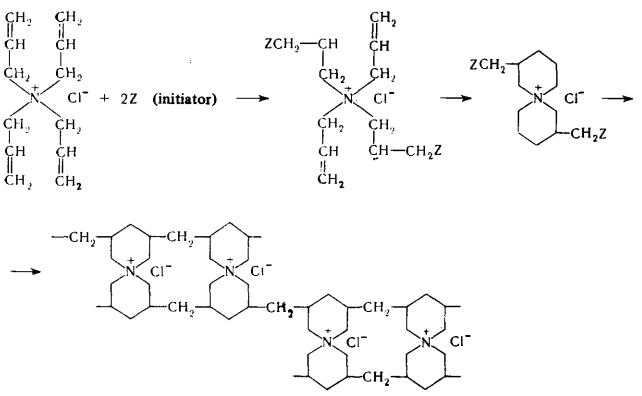


Tevlina et al. [238] first synthesised a water-soluble polymeric base (by the chloromethylation of polystyrene and polyvinyltoluene followed by amination), and then combined it with poly(vinyl alcohol). The resulting films were heated at 120–140°C for 20 h in order to cross-link them. The authors [238] suggest a scheme for formation of the water-soluble polymeric base, but give no mechanism by which the three-dimensional structure is produced. The poly(vinyl alcohol) probably undergoes cross-linking by the formation of ether bonds [360]. It is hardly possible in this case that a cross-linked membrane of homogeneous type could be obtained by interaction of unchanged chlorine in the chloromethyl group with the poly(vinyl alcohol). This is supported also by the fact that the polyelectrolyte is gradually eluted from the membrane [238]. The membranes possess quite low electrical resistance (1–2 ohm cm^{-2}) and an exchange capacity of around 1–2 mg-equiv. g^{-1}. The swelling is greatly dependent on the amount of polyelectrolyte introduced, which usually varied over the range 25–75%.

The swelling in water, and especially in alkaline solutions, was found to increase at polyelectrolyte contents of 50% and above. When it was increased to 75%, the capacity of the membranes dropped sharply after the first regeneration (owing to elution of the water-soluble polymeric base).

Syntheses of anion-exchange membranes have also been suggested from but-3-en-2-one, styrene, and divinylbenzene[312], styrene, divinylbenzene, and butadiene[230], etc.

An interesting synthesis of anion-exchange membranes is based on poly(tetra-allylammonium chloride). The polymer is obtained in aqueous solution in the presence of ammonium persulphate at 50°C, and is treated with triallylamine hydrochloride[197]. The work of Butler et al.[361,362] established that tri- and tetra-allyl derivatives form insoluble three-dimensional structures on polymerisation. They suggest that the mechanism of polymerisation involves radical formation from the initial monomer, intra- and inter-molecular chain transfer, and formation of a three-dimensional polymer from alternating piperidine rings and methylene groups. It is probable that synthesis of the membranes[197] involves also formation of stable six-membered rings, which then undergo cross-linking:



Many polymerisation membranes have not found wide industrial use owing to their low mechanical strength and the difficulty of obtaining large sheets. The following membranes are manufactured by industry—Nepton CR-51, CR-61, and AR-111, Permutit C-1373 and A-1374 (USA); Zerolit C-60, DK-1, A-60, and DA-1 (England); Serion C-100 and A-100 (Japan); MK-100 and MA-100 (USSR); etc.

(c) Activated Films

The chemical modification of inert polymer films is the most convenient way of synthesising ion-exchange membranes, since it is considerably simpler to obtain films from an inert thermoplastic polymer than from a polymer containing ionogenic groups. Furthermore, this method enables very thin membranes to be obtained.

Matrix membranes. The way in which membranes of this type are synthesised is in effect to obtain a film from a copolymer (mostly a styrene–divinylbenzene or a styrene–butadiene copolymer), and then to introduce ionogenic groups into the film.

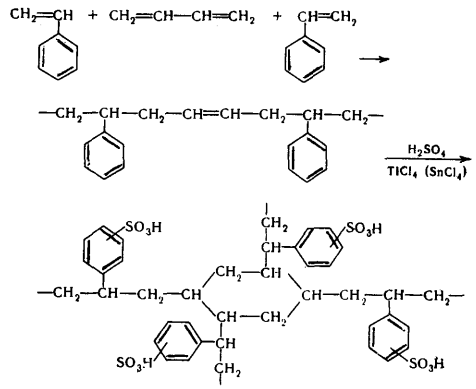
An example is the method proposed by the Japanese chemists Tsunoda and Seko[141], who used a copolymer of styrene, divinylbenzene, and ethylbenzene to form the matrix. The partly polymerised copolymer was dissolved in monomeric styrene, and the reaction completed by heating the mixture in a closed vessel at 100°C for 50 h. The copolymer was sulphonated.

Several analogous membranes have been obtained based on a styrene–divinylbenzene copolymer[142,195].

A ready prepared rubber latex can be used for film formation. The technique of this process is usually to impregnate a reinforcing cloth with a butadiene–styrene latex, dry, and treat with sulphonating or aminating agents. In an example described in a Japanese patent[149], a latex consisting of 29% of styrene and 71% of butadiene is applied to glass fibre, and the dried film is sulphonated with 96% sulphuric acid. Other membranes are obtained similarly[70,130]. The properties of this type of membranes depend on the film thickness, the proportions of styrene and butadiene, the concentration of sulphuric acid, and the time of treatment. The optimum concentration of sulphuric acid is 96%, and the styrene content 40–50%.

Nishihara[79] suggests a synthesis of a cation-exchange membrane which is selective with respect to individual cations. A matrix consisting of glass fibre and a styrene–butadiene latex (1 : 1) is placed in a 25% aqueous solution of resorcinol at 30°C for 20 min, and then in an aqueous solution containing hydrogen chloride (20%) and formaldehyde (15%) at 30°C. After half an hour the membrane is washed with water and 0.5 *N* sodium chloride. The presence of a three-dimensional structure helps to increase selectivity and improve other properties of the membrane[79].

Cyclisation is often used to form a cross-linked structure. Reactions of this type can be accomplished in the presence of such reagents as titanium and tin tetrachlorides. The former is the more effective catalyst, polymers having a greater degree of cross-linking being obtained in its presence, while the membranes are characterised by better electrochemical characteristics. Japanese chemists[189,239] suggest the synthesis of cation- and anion-exchange membranes based on a styrene–butadiene copolymer, cross-linking being effected by cyclisation. An advantage of this method is the simultaneous occurrence of the reactions in a single stage. The mechanism of formation of a cross-linked sulphonated polymer can probably be represented by the scheme



To obtain a strongly basic anion-exchange membrane a film of a copolymer of butadiene with 2-methyl-5-vinylpyridine is treated with methyl iodide. A disadvantage of such membranes is[185] that they can be used only in solutions of pH < 6.

Methods of synthesising matrix membranes have the advantage that a ready made copolymer is usually used, and films of large dimensions are fairly simply obtained. In

most cases, however, the membranes do not possess sufficient mechanical strength for their practical utilisation.

Graft membranes. Membranes having comparatively good electrochemical properties and mechanical strength can be synthesised on the basis of graft polymers formed by attacking the main chain of the polymer with reaction-initiating radicals. In practice initiation by ultraviolet radiation or by a cobalt-60 source is most often employed. The production of radicals by means of peroxide initiators is also widely used. In the synthesis of graft membranes based on polymer matrices and obtained by radiation grafting the source most often used is cobalt-60 [246-259].

Polyethylene, poly(vinyl chloride), polytetrafluoroethylene, etc. films are used as base for radiation grafting. The monomers which are grafted on are styrene [240,245-254], vinylpyridine and its derivatives, methyl acrylate, acrylonitrile [255,265], vinyltoluene, vinylnaphthalene [258], etc.

Ballantine et al. [363] studied the initiation by γ-rays of the formation of graft copolymers from polyethylene films and styrene. Ion-exchange membranes obtained by grafting styrene (20–30%) to polyethylene at a radiation dose of 1.06 Mrad possess the following characteristics [364]: thickness of damp membranes ~ 0.15 mm, exchange capacity 1.2 mg-equiv. g^{-1}, surface electrical resistance in 0.6 N potassium chloride solution 30 ohms cm^{-2}, selectivity 91.0, resistance to tearing in damp state 2.32 kg cm^{-2}, tensile strength in damp state 147.7 kg cm^{-2}, and elongation 190% [364].

Carbon–halogen bonds are more susceptible to attack by a radical and to the reaction of chain transfer than are carbon–hydrogen bonds. Therefore a membrane based on poly(vinyl chloride) is more easily obtained than one based on polyethylene.

In the synthesis of graft polymers, including those used for membranes, various changes produced by the action of radiation—formation of chemical bonds, degradation, oxidation, evolution of gas—are often observed, and these affect the properties of the final products [365].

An interesting generalisation applying to the action of radiation on vinyl polymers, which are usually employed in the synthesis of ion-exchange membranes, was made by Wall [366]: on irradiation in the absence of oxygen, cross-linking processes predominate in polymers having a fairly high heat of polymerisation, whereas degradative processes predominate in polymers possessing a lower heat of polymerisation. The heat of polymerisation is small for stressed molecules (poly-α-methylstyrene) and high for systems having sterically unstressed molecules (polystyrene, polypropylene, polyethylene). This is probably the reason why compounds of the latter type have been suggested almost exclusively for the synthesis of membranes.

Kargin, Cherneva, and their coworkers [71,266] among others have described the preparation of homogeneous graft membranes by initiation with ultraviolet radiation.

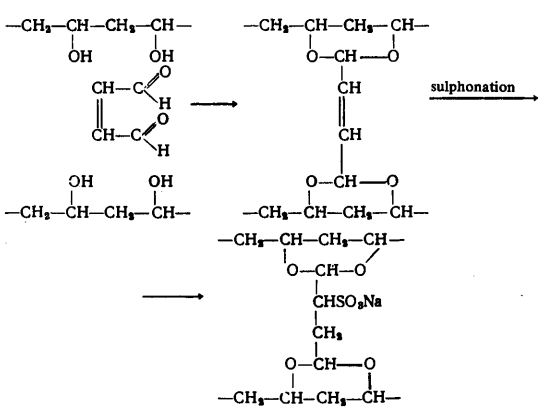
Zenftman [132] proposes the preparation of a graft ion-exchange membrane based on a styrene–polyethylene copolymer. Grafting is conducted in the presence of benzoyl peroxide in an inert gas (nitrogen). Treatment of the matrix with chlorosulphuric acid at 52°C for 30 min yields a cation-exchange membrane having a resistance of 37.7 ohms cm^2 and a selectivity of 0.97.

From a technical point of view the use of radiation polymerisation gives several advantages in comparison with well known methods of polymerisation. In particular, it becomes possible to avoid severe conditions for polymerisation, and unnecessary to employ expensive catalysts, traces of which cannot now contaminate the polymer. Opportunities for controlling the polymerisation process are considerably improved [367]. However, a disadvantage of radiation-grafted membranes is the difficulty of obtaining them under industrial conditions: this method has hitherto been still at the stage of laboratory research. The greatest interest attaches to chemical methods, since they enable graft polymers of desired composition and structure to be obtained in a pure form.

Film membranes. Ready made polymer films—hydrophilic or hydrophobic—are taken in all the proposed methods of synthesising film membranes. An inert film is transformed into an ion-exchange membrane in a single stage. Active groups are introduced by treatment with sulphonating agents, or else by chloromethylation followed by amination. Membranes based on either hydrophilic or hydrophobic films often have diminished mechanical strength.

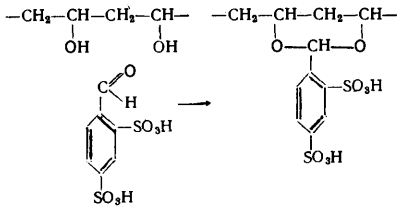
Membranes based on hydrophilic films. A cellulosic material—parchment, cotton cloth, cellulose acetate or regenerated cellulose sheets—or poly(vinyl alcohol) is used as the base. Polyisocyanates, bishydroxymethyladipamide, xanthates, etc. can be used as bridging agents. The use of parchment paper as starting material in the industrial production of large membranes is due mainly to its cheapness and availability. The ability of membranes based on parchment paper to withstand the stresses arising during heat-treatment and on subsequent immersion in water is attributed to the fibrous structure of the cellulosic base. The high water content of membranes of this type leads to low selectivity in relatively concentrated electrolyte solutions; the electrical resistance of such membranes is not large. In spite of the widespread use of membranes of this type, they have several important defects—poor chemical stability, cumbersome mode of production in most cases, etc.

Hydrophilic films of poly(vinyl alcohol) and cellulose can be modified in various ways, the most suitable being acetalisation or etherification of the hydroxyls with compounds containing ionogenic groups [158,173,176,275-286]. Cation-exchange membranes based on poly(vinyl alcohol) are obtained by treatment of the film under mild conditions with malealdehyde followed by addition of sodium hydrogen sulphite [158]:



The strength of the specimens obtained exceeds that of viscose rayon fibres, but the exchange capacity is around 0.2–0.25 mg-equiv. g^{-1} [158]. A greater effect is achieved

by using 4-formylbenzene-1,3-disulphonic acid:



Treatment with formaldehyde makes the membranes insoluble in water. The exchange capacity reaches 0.5–1.0 mg-equiv. g^{-1} [158].

Weakly acid membranes are obtained by heating a high-viscosity poly(vinyl alcohol) in a current of oxygen at 175°C for 5–15 min. Degradation is accompanied by an increase in crystallinity, cleavage of the chains, cross-linking, and oxidation to ketonic and carboxylic groups. Membranes obtained by the thermo-oxidative degradation of poly(vinyl alcohol) under milder conditions are less selective [173].

Weakly acid membranes are obtained by treating sheets of cellulose with an aqueous solution of phosphates of poly(vinyl alcohol) and then heating without a catalyst at 150°C for 15 min [176]. Treatment of poly(vinyl alcohol) films with various aliphatic, aromatic, and heterocyclic amines yields anion-exchange membranes [150,177,194]. The action of pyridine on a dry poly(vinyl alcohol) film at 100°C for 2 h gives a membrane having a low resistance. Insolubility in water (cross-linking) is effected by treating the final product with an organic polyisocyanate [177].

Membranes based on hydrophobic matrices. In this case industrial films of polystyrene, polyethylene, poly(vinyl chloride), polychlorotrifluoroethylene, and several others serve as base for the membranes. Ionogenic groups are introduced by direct sulphonation or amination of the film. The reagents usually employed in these reactions are hydrophilic in character and it is difficult to combine them with a hydrophobic film of compact structure. A further series of difficulties arise in the preparation of such membranes. For example, if the initial hydrophobic films are more than 0.07–0.08 mm thick, a very long time (usually exceeding 24 h) is required for complete swelling of the film. Thinner films are easily deformed, and the membranes obtained have poor mechanical strength. These difficulties, which usually occur in the chemical treatment of hydrophobic sheet material, can probably be overcome by using agents which promote swelling, or plasticisers, the presence of which facilitates sulphonation and has a favourable effect on the mechanical properties of the membranes. Phthalates are most often used as the plasticisers.

Cation-exchange membranes are obtained predominantly by sulphonation, more rarely by phosphorylation. Anion-exchange membranes are produced by chloromethylation of aromatic rings followed by amination or, in the case of halogenated polymer films, by direct amination.

Polystyrene films is the most convenient from the point of view of reprocessing and the chemical stability of the resulting membranes. Westermark [140] prepared a cation-exchange membrane by treating sheet polystyrene with sulphuric acid mixed with an organic solvent. The action of a strong sulphonating agent (e.g. chlorosulphuric acid) effects cross-linking through sulphonyl bridges. A disadvantage of these membranes is their poor mechanical strength.

Abrams and Adrian [178] obtained anion-exchange membranes from sheet polystyrene by the action of a mixture of formaldehyde, a polar organic liquid containing oxygen, and a halogenated sulphonic acid. This mixture forms a complex capable of cross-linking a linear polystyrene matrix. At the same time active groups are included in the polymer structure, and these can be subsequently transformed into quaternary bases by treatment with the appropriate amines. A negative aspect of this method is that the complex of the halogenated sulphonic acid with formaldehyde gradually ages.

Polyethylene [168,287–292] and poly(vinyl chloride) [77,293–297] films are most often used as the hydrophobic base. In view of the chemical resistance of these films to the action of sulphuric acid, sulphonation is accomplished predominantly with strongly acting agents (chlorosulphuric acid, oleum, sulphuryl chloride).

Vasil'ev et al. [289] prepared homogeneous membranes by sulphonating polymer films, and investigated the possibility of their use in electrochemical processes. Films of high-pressure polyethylene were sulphonated with sulphuric acid, oleum, or chlorosulphuric acid at 30°C; the resistance of the membrane was 20 ohm cm^{-2} in 10 *N* potassium hydroxide solution, and its exchange capacity 1.5 mg-equiv. g^{-1}. At 40°C chlorosulphuric acid destroys the film. Low-pressure polyethylene is broken down by chlorosulphuric acid above 50°C, but at 45–50°C sulphonation yields a membrane having an exchange capacity of 4 mg-equiv. g^{-1}. The crystallinity of polyethylene is preserved during sulphonation for 2 h, but is completely destroyed at 50°C after 4 h. Transition of the crystalline into an amorphous structure probably accompanies sulphonation throughout the thickness of the films, as is proved by the sharp increase in the electrical conductivity of the membranes. Degradation of the polyethylene is also possible, of course. The investigations made it clear that the homogeneous membranes obtained could have no practical application owing to their inadequate mechanical strength, chemical stability, and electrical conductivity.

Improvement in mechanical and chemical stability is achieved when the matrix of the membrane consists of polymeric chlorotrifluoroethylene or tetrafluoroethylene, but these membranes exhibit a tendency to intermembrane deposits.

Membranes based on poly(vinylidene fluoride) have been described. Direct sulphonation of a film of the latter takes place mainly on the surface owing to the difficulty of access by the sulphonating agent to the interior of the polymer. Sulphonation of a previously swollen film of the same material takes place throughout the film. In the latter case the rate of sulphonation is increased, and a membrane of relatively low electrical resistance is obtained [254].

The synthesis of ion-exchange membranes based on hydrophobic films has not become widespread. This is because the introduction of ionogenic groups into inert films takes place under severe conditions (high temperature, strong sulphonating agents, etc.) and causes degradation of the polymer. Owing to the difference in chemical nature between the film and the reagent introducing the active groups, the distribution of the latter in the membrane is non-uniform. This has an unfavourable effect on the electrochemical properties of the resulting membranes, which in most cases have a high resistance and low selectivity.

3. INTERPOLYMER MEMBRANES

Increasing attention has been paid during recent years to this type of membranes, because of their interesting combination of properties. Several of them possess

excellent electrochemical characteristics together with satisfactory mechanical strength. Interpolymer membranes are closely similar to homogeneous membranes in properties and structure, since the macromolecules of polyelectrolyte and inert polymer are closely interlinked and appear to form one phase, although chemical bonds are not usually formed. The interlinking of the active component of the membrane with the inert component should hinder and practically exclude its elution during operation. However, the absence of cross-linking bridges may be a reason for gradual partial elution of the active component.

Dynel Membranes

These membranes obtained their name from the original product "dynel" (a copolymer of vinyl chloride and acrylonitrile)[70,76,169]. Poly(styrenesulphonic acid), poly(acrylic acid), a copolymer of maleic acid and methyl vinyl ether, polyvinylimidazole, polyamines, etc. are used as the polyelectrolyte. A mixture of the two polymers is dissolved in a solvent for both hydrophilic polyelectrolytes and hydrophobic inert polymers, this requirement being met by dimethylformamide, dimethyl sulphoxide, and γ-butyrolactone.

Dynel membranes were first synthesised by Gregor and his coworkers[18,19]. A cation-exchange membrane was synthesised by dissolving poly(styrenesulphonic acid) (23%) and dynel (77%) in a mixture of cyclohexanone and methanol, and then pouring the film at 50°C and removing the solvent. For the synthesis of an anion-exchange membrane it is proposed to dissolve a linear poly(vinylbenzyltrimethylammonium chloride) (27%) with dynel in the same solvents. Such a membrane possesses an electrical resistivity of 200–300 ohm cm in 0.1 *N* sodium chloride and a selectivity of around 99%.

The difficulty of producing dynel membranes of large dimensions, the consumption of large quantities of solvents, the complexity of obtaining pure polyelectrolytes, and the relatively low electrical conductivity of the synthesised specimens create obstacles to their industrial utilisation.

Lyubman, Shostak, and their coworkers[316-329] suggested original syntheses of the interpolymer membranes Ankalit K-1 and K-2. The former are obtained by blending polystyrene and polyethylene on rolls in the presence of a hydrocarbon–formaldehyde resin, which functions as both cross-linking agent and plasticiser, lowering the melting points of both polymers. The electrical resistivity of the membrane does not exceed 130 ohm cm[316]. The K-2 membranes were synthesised by dissolving poly(vinyl chloride) and styrene–formaldehyde resin in a common solvent and then pouring the film. Introduction of ionogenic groups (sulphonation) takes place at the same time as cross-linking. The cross-linking–sulphonating reaction takes place at low temperatures of 0–20°C[320]. Introduction of a sulphogroup into the polymer at high temperatures (80–100°C) has an adverse effect on the strength of the membranes. Ankalit K-2 membranes are noteworthy in this respect, their synthesis involving rapid cross-linking at temperatures close to 0°C.

Activated Interpolymer Membranes

These membranes have been acquiring increasing importance during recent years. Combining a ready made inert polymeric film with a monomer which is activated by further treatment may yield mechanically strong membranes possessing adequate electrochemical characteristics.

Polystyrene[74,309,311], a copolymer thereof with divinylbenzene[306,308,310,313,315] or with butadiene[184,185], or a copolymer of styrene, divinylbenzene, and but-3-en-2-one[312] is usually taken as the polymer into which ionogenic groups are introduced. Polyethylene[306-310,316,317], poly(vinyl chloride)[311,315,332], polypropylene[303], and poly(vinylidene chloride)[313,314] are used in the form of films.

The synthesis of interpolymer membranes by the activation of a ready made thermoplastic film is accomplished by impregnating the initial polymer in a monomer or a mixture of monomers, polymerising (or copolymerising) the latter within the film in the presence of an initiator, and introducing ionogenic groups by the usual methods.

Activated interpolymer membranes will probably be given the principal role in electrodialysis processes, although at the present time most of them possess insufficiently low electrical resistance (~ 150–300 ohm cm). The above methods do not ensure good electrochemical characteristics, and moreover membranes of great mechanical strength are rarely obtained.

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In spite of the great scope of the investigations, the problem of synthesising ion-exchange membranes remains unsolved. The effective life of even the best of them does not exceed 3–5 years, whereas for a granular exchanger it sometimes reaches 15 years. No practical methods have been developed for synthesising membranes possessing selective properties towards individual ions of the same sign. Theoretical investigations on membrane processes considerably outstrip corresponding researches on the synthesis of membranes. An urgent problem is also the production of biologically active membranes, which might fulfil the functions of membranes in animal and vegetable organisms.

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Sulphur-containing Organic Compounds of Boron

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This article gives the present state of the chemistry of the organic compounds of boron which include sulphur in their composition. Methods of preparation and the chemical properties of the ortho- and meta-thioborates, esters of halogenothioboric acids, esters of organothioboric acids, alkylthio-1,3,2-dioxaborolanes, 1,2-thiaborolanes, *B*-alkylthio-derivatives of borazole, alkylthioboranes, and dialkylamino(alkylthio)boranes are examined. The sulphur-containing boron compounds exhibit high reactivity and many types of compounds with B–S bonds which are now readily available are used successfully for the synthesis of the most diverse classes of organoboron compounds, including various boron–nitrogen heterocyclic systems and boron-containing polymers. The esters of thioboric and organothioboric acids also find application for the synthesis of organosulphur compounds. There is a bibliography of 124 references.

CONTENTS

I.	Introduction	935
II.	Ortho- and meta-thioborates	935
III.	Esters of organothioboric acids	937
IV.	*B*-Alkylthioborazoles	944
V.	1,2-Thiaborolanes	946
VI.	Alkylthioboranes	946
VII.	Dialkylamino(alkylthio)boranes	950

I. INTRODUCTION

The first mention of sulphur-containing organic compounds of boron dates from 1878, when Councler[1] obtained from tri-isobutyl borate and phosphorus(V) sulphide a compound which was taken to be tri-isobutyl thioborate. From 1908 [2] for half a century the investigations in this field were carried out sporadically and only became systematic in 1959. This division of boron chemistry can now be regarded as comparatively well studied. There are simple and preparatively convenient methods for the synthesis of the main types of compound with B–S bonds, such as thioborates, esters of organothioboric acids, alkylthioboranes, compounds with mixed functions, and sulphur-containing heterocyclic boron compounds of various types. The chemical properties of sulphur-containing organoboron compounds have been rather widely studied.

The problems of the chemistry of sulphur-containing boron compounds has been partly covered in a review article[3] and in Gerrard's book[4]. Compounds with B–S bonds but not containing B–C bonds were examined in Steinberg's book[5] published in 1964.

II. ORTHO- AND META-THIOBORATES

As a result of the reaction of tri-isobutyl borate with phosphorus(V) sulphide a yellow substance was obtained, which was assumed to be slightly impure tri-isobutyl thioborate[1]. It is very doubtful, however, whether this substance was a thioborate, since it decomposed in a vacuum, whereas alkyl thioborates distil without decomposition. The first representative of the esters of thioboric acid—trimethyl thioborate—was made in 1952 by the action of silver or lead hydrogen sulphide on boron tribromide[6].

A. METHODS OF PREPARATION

1. Synthesis of Thioborates from Boron Trihalides

The most convenient and economic method for obtaining thioborates consists in the action of thiols on boron trichloride:

$$BCl_3 + 3\,RSH \rightarrow B(SR)_3 + 3\,HCl\,.$$

Despite the apparent simplicity of this reaction, the first attempts to use it for the synthesis of thioborates were unsuccessful. Thus as a result of the reaction of boron trichloride and methanethiol, methylthioboron dichloride was obtained as the dimer $(CH_3SBCl_2)_2$, which does not react further with the thiol[6]. The reaction with thiophenol also does not go to completion[7]. As was shown later, all the chlorine atoms can be replaced by alkylthio-groups under more severe conditions. On mixing boron trichloride and thiols in the cold, crystalline complexes

$$Cl_3B \cdot S\begin{matrix}R\\H\end{matrix},$$

are formed, which lose a molecule of hydrogen chloride at 0–40°C. On carrying out the reaction with higher thiols, which have a rather high boiling point, subsequent heating of the reaction mass at 80–150°C gave alkylthioborates[8]. Propyl thioborate (30%) and butyl thioborate (67%) were obtained by this method. Pentyl thioborate was obtained in 57% yield by boiling a decane solution of boron trichloride and pentanethiol[9].

The reaction of boron trichloride with thiols in the presence of tertiary amines or pyridine proceeds more smoothly. When the reaction is carried out without heating, the yields of thioborates under these conditions are moderate. Thus, in the care of boron trichloride and methanethiol in pentane at 0°C in the presence of trimethylamine the yield of trimethyl thioborate was only 34%.[9] However, on boiling an ethereal solution of a mixture of methanethiol, boron trichloride, and triethylamine for 2 h trimethyl thioborate could be obtained in 80% yield. The reaction with other thiols also proceeds smoothly (yields of 70–90%)[8]:

$$BCl_3 + 3\,RSH + 3\,R'_3N \rightarrow B(SR)_3 + 3R'_3NHCl\,.$$

The reactions of boron tribromide with thiols were also investigated. With methanethiol BBr_3 forms a monosubstituted compound—the dimer of methylthioboron dibromide[6,10]; reaction with pentane-1-thiol in the presence of pyridine leads to pentyl thioborate in 27% yield[9]; with thiophenol, triphenyl thioborate is obtained[7,11].

Thioborates can be obtained by the action of metal mercaptides on boron trihalides. Trimethyl thioborate is synthesised by boiling a benzene solution of boron trichloride and silver or lead hydrogen sulphide (but not potassium hydrogen sulphide)[6] or by heating BBr_3 with sodium hydrogen sulphide without a solvent[12].

By starting from boron tribromide with silver thiocyanate, boron thiocyanate was synthesised[2], which was subsequently assigned the isothiocyanate structure[13].

2. Synthesis of Thioborates on the Basis of Diborane

The trimers of the alkylthioboranes (1,3,5-cyclotriborathianes) obtained by the action of thiols on diborane react at 100–120°C with thiols to form alkyl thioborates[14]:

$$(RSBH_2)_3 + 6\,RSH \xrightarrow{100-120^\circ} 3\,B(SR)_3 + 6\,H_2\,.$$

Alkyl thioborates can also be obtained by heating di(alkylthio)boranes[15,16] or trialkylamine–boranes[17,18] with thiols:

$$(RS)_2BH + RSH \xrightarrow{60-150^\circ} B(SR)_3 + H_2$$

$$H_3B \leftarrow NR_3 + 3\,RSH \xrightarrow{60-100^\circ} B(SR)_3 + NR_3 + 3\,H_2\,.$$

3. Various Reactions in Which Orthiothioborates, Their Derivatives, and Metathioborates Are Formed

A series of reactions are known, mostly not of preparative value, as a result of which thioborates are formed.

The reaction of methanethiol, hexanethiol, or phenylmethanethiol and hydrogen chloride with tris(dialkylamino)-boron gave the corresponding thioborates[9,19].

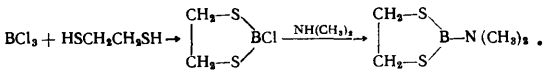
Ethyl thioborate was obtained by the action of hydrogen sulphide on ethylthioboron dibromide[20]:

$$3\,C_2H_5SBBr_2 + 3\,H_2S \rightarrow B(SC_2H_5)_3 + B_2S_3 + 6\,HBr\,.$$

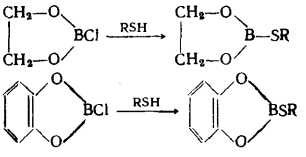
The polymer of methylthioborane undergoes disproportionation into methyl thioborate and diborane at 140°C;[12] trimethylamine–methylthioborane[12] and the methyl esters of methyl- and dimethyl-thioboric acids[21] also disproportionate (145°C) to methyl thioborate. Triphenyl thioborate was obtained by the reaction of potassium tetrafluoroborate and tris(phenylthio)aluminium[22]:

$$KBF_4 + Al(SC_6H_5)_3 \xrightarrow{240^\circ} B(SC_6H_5)_3 + AlF_3 + KF\,.$$

The action of ethane-1,2-dithiol on boron trichloride gave 2-chloro-1,3,2-dithiaborolane, which was converted into the dimethylamino-derivative[23]:

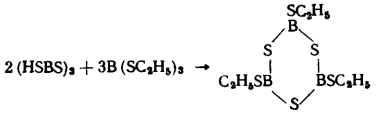


2-Alkylthio-1,3,2-dioxaborolanes are obtained from the corresponding chloro-derivatives and thiols[24–26]:



where R = n-C_4H_9 or n-C_8H_{17}.

Prolonged boiling of a carbon disulphide solution of metaboric acid[27,28] and triethyl borate gives a trimer of an ester of metaboric acid[29]:



which is converted on distillation into the dimer $(C_2H_5SBS)_2$.

B. PROPERTIES

Trialkyl thioborates are liquids with a very unpleasant odour; triphenyl thioborate is a solid melting over a wide range.

The ^{11}B chemical shift in tributyl thioborate is –47.9 p.p.m. in relation to trimethyl borate[17]. Thioborate exhibits an intense absorption band in the 10–11 μm range and a weaker one in the 13.25–13.50 μm range.

1. Hydrolysis and Alcoholysis

Thioborates are readily hydrolysed by water with the formation of boric acid and thiols[12,17]; with alcohols they give alkyl borates and thiols[6]:

$$B(SR)_3 + 3\,ROH \rightarrow B(OR)_3 + 3\,RSH\,.$$

2. Reactions with Amines

Trimethyl thioborate and pyridine form a 1 : 1 adduct[8]; triethyl thioborate gives an unstable complex with pyridine, which decomposes on heating into the initial components[30].

As the example of triethyl thioborate showed, the reaction of thioborates with primary or secondary amines proceeds by successive replacement of alkylthio-groups by the corresponding alkylamino-groups and as a result, depending on the ratio of the reagents, the products[30] are *N*-substituted bis(alkylthio)aminoborane, an alkylthiodiaminoborane, or triaminoborane, unchanged on distillation:

$$B(SC_2H_5)_3 + RR'NH \rightarrow RR'NB(SC_2H_5)_2 + C_2H_5SH\,,$$
$$B(SC_2H_5)_3 + 2\,RR'NH \rightarrow (RR'N)_2BSC_2H_5 + 2\,C_2H_5CH\,,$$
$$B(SC_2H_5)_3 + 3\,RR'NH \rightarrow (RR'N)_3B + 3\,C_2H_5SH\,,$$

where R = H or Alk.

Bis(ethylthio)phenylaminoborane, obtained by the action of 1 mole aniline on triethyl thioborate, is symmetrised at room temperature into tris(phenylamino)boron and triethyl thioborate.

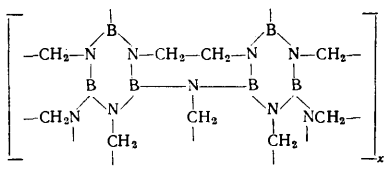
The compound $[(CH_3)_2NBS]_3$ which is a trimer of the anhydride of dimethylaminothioboric acid, is synthesised by the action of tris(dimethylamino)boron on metathioboric acid[31,32] or the anhydride of bromothioboric acid[32] and also from metathioboric acid and $Al[N(CH_3)_2]_3$:[33]

$$(HSBS)_3 + B[N(CH_3)_2]_3 \rightarrow [(CH_3)_2NBS]_3 + B(SH)_3\,,$$
$$(BrBS)_3 + B[N(CH_3)_2]_3 \rightarrow [(CH_3)_2NBS]_3 + BBr_3\,.$$

$(CH_3NHBS)_3$ was also obtained by the action of methylamine on $(BrBS)_3$:[20]

$$(BrBS)_3 + 3NH_2CH_3 \rightarrow (CH_3NHBS)_3 + 3HBr\,.$$

The action of ethylenediamine on triethyl thioborate (1 : 1) gives a polymer which does not contain ethylthio-groups and to which is ascribed the structure[30]:



3. Exchange Reactions with Boron Compounds

Trialkyl thioborates undergo exchange reactions with esters of organoboron acids[34-36] or boron trialkyls[21,34,37], as a result of which esters of organothioboron acids are formed. These conversions are a method for the synthesis of the last class of compound, considered in Section III, A, 3.

4. Reactions with Carbonyl Compounds and Vinyl Esters

The high reactivity of thioborates appears in their reactions with various organic compounds, such as aldehydes, ketones, amides of acids, and vinyl esters.

Trialkyl thioborates react with aldehydes and ketones to form thioacetals or thioketals and boron sesquioxide[38]. The reaction between triethyl thioborate and benzaldehyde in benzene solution is exothermic and yields boron sesquioxide and the bis(ethylthio) acetal of benzaldehyde in 91% yield:

$$3C_6H_5CHO + 2B(SC_2H_5)_3 \rightarrow 3C_6H_5CH(SC_2H_5)_2 + B_2O_3\,.$$

On heating a benzene solution of acetone and tributyl thioborate, the bis-(n-butylthio) ketal of acetone is formed in 90% yield:

$$3CH_3COCH_3 + 2B(SC_4H_9)_3 \rightarrow 3(CH_3)_2C(SC_4H_9)_2 + B_2O_3\,.$$

Under similar conditions triethyl thioborate and acetophonone give acetophenone diethylthio ketal smoothly.

The process evidently proceeds by the addition of thioborate at the carbonyl group:

$$R_2CO + B(SR)_3 \rightarrow R_2C\begin{matrix}OB(SR)_2\\SR\end{matrix}$$

and further conversion of the addition product by the scheme:

$$R_2C\begin{matrix}OB(SR)_2\\SR\end{matrix} + B(SR)_3 \rightarrow R_2C(SR)_2 + (RS)_2BOB(SR)_2\,.$$
$$\downarrow B(SR)_3 + B_2O_3$$

Dimethylformamide reacts like aldehydes and ketones with thioborates[39]:

$$3(CH_3)_2NCHO + 2B(SC_4H_9)_3 \rightarrow (CH_3)_2NCH(SC_4H_9)_2 + B_2O_3\,.$$

The comparatively high yield (66%) of bis(butylthio)-dimethylaminomethane shows the possibility of using this reaction for the preparation of amidomercaptals.

On heating thioborates with vinyl esters, alkyl vinyl sulphides and alkyl borates are obtained[39]:

$$3CH_2{=}CHOR + B(SR)_3 \xrightarrow{100-150^\circ} CH_2{=}CHSR + B(OR)_3$$

Butyl vinyl sulphide was obtained in 71% yield from tributyl thioborate and butyl vinyl ether by this method. Tripropyl thioborate and butyl vinyl ether react similarly, as do tributyl thioborate and ethyl vinyl ether.

It must be assumed that the thioborate adds at the double bond of the vinyl ether and the addition product then undergoes β-decomposition with the elimination of an alkyl vinyl sulphide:

$$CH_2{=}CHOR + B(SR)_3 \rightarrow (RS)_2BCH_2CH\begin{matrix}OR\\SR\end{matrix} \rightarrow$$
$$\rightarrow (RS)_2B\begin{matrix}O-CH-SR\\|\\CH_2\end{matrix} \rightarrow (RS)_2BOR + CH_2{=}CHSR\,.$$
$$\downarrow B(OR)_3 + B(SR)_3$$

This mechanism for the reaction agrees well with the tendency of β-alkoxy-derivatives of alkylboron acids to eliminate ethylene[40].

III. ESTERS OF ORGANOTHIOBORIC ACIDS

Like thioborates, esters of organothioboric acids have attracted attention only in recent years. The first representatives of this class of compounds—the dodecyl and

octyl esters of 2-chlorovinylthioboric acid—were obtained[41] in 1946. Several other representatives of this class of compound were described subsequently but systematic study of the esters of organothioboric acids only began in 1959. Preparative methods for their synthesis are based on the use of organoboron halides, boron trialkyls, and esters of organoboron acids. The esters of organothioboric acids are, like the thioborates, very reactive substances, and are used successfully for the synthesis of various classes of boron compounds.

A. METHODS OF PREPARATION

1. Synthesis of Esters of Organothioboric acids from Organoboron Halides

One of the general methods of synthesis of esters of organothioboric acids consists in the action of thiols or metal mercaptides on organoboron halides. This method allows esters of organothioboric acids of the aliphatic and aromatic series to be obtained.

Octyl (2-chlorovinyl)chlorothioborate was first obtained by this method from octanethiol and 2-chlorovinylboron dichloride[41]. It was found subsequently that the replacement of one or both halogen atoms in alkylboron dihalides by an alkylthio-group depends on the ratio of the reagents, the temperature, and the duration of heating.

On boiling a mixture of an alkylboron dichloride or alkylboron dibromide with an excess of butane-1-thiol for 10–15 h, n-butyl alkylthioborates are formed smoothly[42]:

$$RBX_2 + 2n\text{-}C_4H_9SH \rightarrow RB(SC_4H_9\text{-}n)_2 + 2HX.$$

n-Butyl phenylthioborate is obtained similarly from phenylboron dichloride[42].

On heating mixtures of alkylboron dichlorides with an excess of ethanethiol, in addition to the diethyl esters of the alkylthioboric acids, products of the incomplete replacement of chlorine atoms are also formed—ethyl esters of (alkylthio)chloroboric acids[43].

$$RBCl_2 \xrightarrow{C_2H_5SH} RB(SC_2H_5)_2 + RBCl(SC_2H_5).$$

Esters of (alkythio)chlorothioboric acids undergo partial symmetrisation into esters of alkylthioboric acids and alkylboron dichlorides when distilled in a vacuum so that esters of alkylchlorothioboric acids cannot be obtained in high yields even in experiments with an equimolecular ratio of the reagents.

Ethyl esters of alkylbromothioboric acids are obtained in 65–75% yields by the reaction of alkylboron dibromides with ethanethiol in 1 : 1 ratio[43]:

$$RBBr_2 + C_2H_5SH \rightarrow RBBr(SC_2H_5) + HBr.$$

Bromothio-esters have a much greater thermal stability than chlorothio-esters and can be distilled in a vacuum without decomposition. Phenylboron dibromide undergoes a similar reaction with ethanethiol[43].

The preparation of esters of alkylchlorothioboric acids can also be effected by an exchange reaction between alkylboron dichlorides and the esters of alkylthioboric acids[43]. Thus, when an equimolecular mixture of n-propylboron dichloride and diethyl n-propylthioborate is left at room temperature for 20 h then by distilling the reaction mixture the ethyl chloro(propyl)thioborate can be isolated in 50% yield.

$$n\text{-}C_3H_7BCl_2 + n\text{-}C_3H_7B(SC_2H_5)_2 \rightarrow 2n\text{-}C_3H_7B(SC_2H_5)Cl.$$

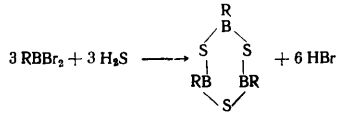
The difference in stability of the esters of the organo-(halogeno)thioboric acids and their oxygen analogues merits attention. Among the compounds of the latter class the tendency to disproportionation is observed only in the esters of organofluoroboric acids[44], whereas the esters of chloro- and bromo-organic acids distil unchanged[45,46].

Yet another method for obtaining esters of alkyl(halogeno)organothioboric acids must be mentioned, consisting in the action of boron halides on the esters of alkylthioboric acids at room temperature[43]. Thus n-butyl isopentylthioborate and boron tribromide gave n-butyl isopentylbromothioborate [bromo(butylthio)isopentylborane]:

$$3iso\text{-}C_5H_{11}B(SC_4H_9\text{-}n)_2 + BBr_3 \xrightarrow[80\%]{} 3iso\text{-}C_5H_9B(SC_4H_9\text{-}n)Br + B(SC_4H_9\text{-}n)_3.$$

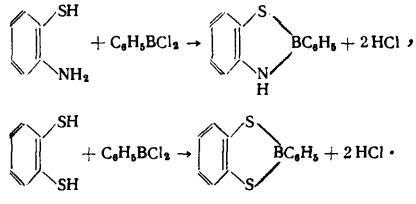
Dialkylboron halides[21,47] and diarylboron halides[42] are converted into the esters of dialkyl- and diaryl-thioboric acids respectively on heating with thiols. In this method various metal mercaptides can be used instead of thiols. Thus the di-n-pentyl ester of phenylthioboric acid [phenyldi(pentylthio)borane] was synthesised by the reaction of phenylboron dichloride with methylthiosodium[48].

When heated with hydrogen sulphide in an inert solvent (benzene, carbon disulphide), phenylboron dibromide[49] and alkylboron dibromides[20] are converted respectively into the anhydrides of phenyl- or alkyl-thioboric acids, which exist as cyclic trimers:



where R = n-C_4H_9, iso-C_4H_9, or C_6H_5.

Cyclic esters of organothioboric acids are formed in the reaction of organoboron dihalides with *ortho*-thio-derivatives of benzene. Thus phenylboron dichloride and 2-aminothiophenol or dithiocatechol gave 2-phenylbenzo-1,3,2-thiazaborolane and 2-phenylbenzo-1,3,2-dithiaborolane respectively[50]:



2. Synthesis of Esters of Organothioboric Acids from Boron Trialkyls

a. Use of thiols. A simple method of obtaining esters of dialkylthioboric acids is the reaction between boron trialkyls and thiols[51,53]. The reaction starts at room temperature and is accompanied by evolution of heat; additional heating of the reaction mass at 110–160°C is necessary to complete the process:

$$BR_3 + R'SH \rightarrow R_2BSR' + RH.$$

A detailed study of this reaction disclosed that it is initiated by peroxide compounds in ultraviolet light[54]. Only freshly distilled boron trialkyls, which almost always contain traces of peroxy-compounds >BOOR, start to react with thiols at room temperature. Furthermore, boron trialkyls freed from peroxides (by heating at 100°C for a few

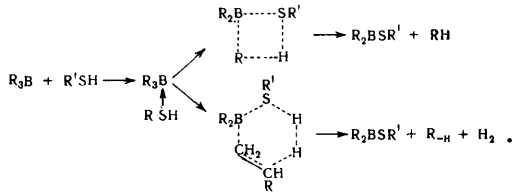
hours or by keeping at room temperature for a few months) do not react with thiols below 150°C. When a little (2–10 ml) air or pieces of porcelain or diatomaceous brick is introduced into a mixture of such "deactivated" boron trialkyls and a thiol a reaction starts, accompanied by the formation of a thioester R_2BSR and an alkane. Reaction takes place at a still greater rate on adding drops of hydrogen peroxide or an alkyl hydroperoxide to the mixture.

The peculiarities of the behaviour of thiols in relation to boron trialkyls, sharply distinguishing them from other nucleophilic reagents, such as water, alcohols, and amines, with which boron trialkyls react at 150–200°C,[51] are explained evidently by the ability of thiols to participate in radical processes brought about by organoboron peroxides.

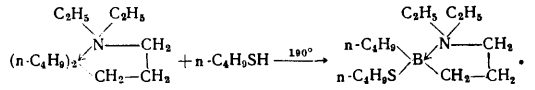
Unlike thiols, thiophenol[51,52] reacts with boron trialkyls on heating and in addition to saturated hydrocarbons the products include alkenes and hydrogen, as when other nucleophilic reagents are used[52]:

$$BR_3 \xrightarrow[150-170^\circ]{C_6H_5SH} R_2BSC_6H_5 + RH + R_{-H} + H_2 .$$

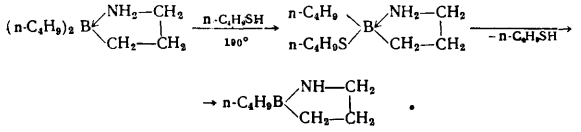
Evidently the formation of saturated hydrocarbons in this reaction occurs through a four-centre transition state, whereas the alkene and hydrogen are obtained by a six-centre mechanism:



It is interesting that mercaptans are capable of reacting with inner complexes of boron trialkyls, but only at a high temperature (190°C). Thus in the action of butane-1-thiol on 3-(diethylamino)propyldibutylboron butyl butyl-3-(diethylamino)propylborate is obtain in 55% yield:



3-Aminopropyldibutylboron also reacts with thiols at high temperature, but the ester of 3-aminopropylbutylthioboric acid formed as an intermediate is immediately converted with loss of a thiol into 2-n-butyl-1,2-azaborolidine[55]:



An increased ability to exchange a radical by an alkylthio-group is exhibited by triallylboron[56,57], which reacts with ethanethiol at temperatures between −10° and −15°C; at an equimolecular ratio of the reagents ethyl diallylthioborate and propene are formed. In the action of 2 moles ethanethiol on 1 mole triallylboron the main reaction product is diethyl allylthioborate but in addition ethyl diallylthioborate and ethyl 3-ethylthiopropylthioborate are obtained:

$$B(CH_2CH=CH_2)_3 + 2\,C_2H_5SH \rightarrow CH_2=CHCH_2B(SC_2H_5)_2 + 2\,C_3H_6$$
$$\downarrow C_2H_5SH$$
$$C_2H_5-S-CH_2-CH_2CH_2B(SC_2H_5)_2 .$$

Diethyl 3-ethylthiopropylthioborate can be obtained by the direct action of ethanethiol on diethyl allylthioborate.

The high reactivity of triallylboron in relation to thiols and also to other nucleophilic reagents[58–61] is evidently connected with an allyl rearrangement in these compounds. As investigation by proton magnetic resonance showed[62], the allyl rearrangement in triallylboron:

$$(C_3H_5)_2\overset{\bullet}{B}CH_2CH=CH_2 \rightleftarrows \overset{\text{transition state}}{\rightleftarrows} (C_3H_5)_2BCH_2CH=\overset{\bullet}{C}H_2$$

proceeds with a velocity from 4.7 Hz at −25°C to 3.3 kHz at 88°C, that is, the average life time of each state varies in this temperature range from 2×10^{-1} to 3×10^{-4} s.

b. Use of Sulphur. One of the features of boron trialkyls is their ability to react with oxygen to form esters of dialkyl- or alkyl-boric acids, depending on the condition. It seemed that sulphur is also capable of reacting with boron trialkyls on heating with formation of esters of dialkylthioboric acids[63,64]:

$$BR_3 + S \xrightarrow{140^\circ} R_2BSR .$$

c. Use of thioborates. At elevated temperatures boron trialkyls enter into an exchange reaction with thioborates to form esters of organothioboric acids. Methyl dimethylthioborate was obtained by this method on prolonged heating of methyl thioborate with trimethylboron in the presence of traces of diborane[21]:

$$2\,B(CH_3)_3 + B(SCH_3)_3 \rightleftarrows 3\,(CH_3)_2BSCH_3 .$$

By heating a 1 : 2 mixture of boron trialkyls and ethyl thioborate for 30–35 h at 250°C ethyl alkylthioborates were obtained in 65–75% yields[37]:

$$BR_3 + 2\,B(SC_2H_5)_3 \xrightarrow{250^\circ} 3\,RB(SC_2H_5)_2 .$$

The reaction of boron trialkyls with butyl thioborate under similar conditions proceeds less smoothly.

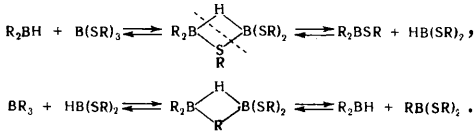
In the reaction products there is a certain amount (10–15%) of an ester of a dialkylthioboric acid and also the initial compounds, which is explained by the reversibility of the reactions:

$$BR_3 + B(SR')_3 \rightleftarrows R_2BSR' + RB(SR')_2 ,$$
$$R_2BSR' + B(SR)_3 \rightleftarrows 2\,RB(SR')_2 .$$

In the reaction with triethyl borate the equilibrium is shifted to the right to a greater extent than in that with tributyl thioborate.

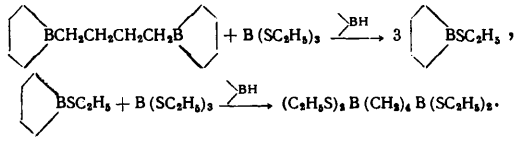
The use of tetra-alkyldiborane as a catalyst allows a much lower temperature and a shorter reaction time to be used in the reaction of tributylboron with tributyl thioborate. The yield of dibutyl butylthioborate was 73%.[34]

The catalytic action of tetra-alkylboranes and also other compounds with B–H bonds, just as in exchange reactions between boron trialkyls and orthoborates[34,65–67], explains their ability to form dimeric intermediate compounds with three-centre B–H–B bonds, for example:



In the presence of compounds with B–H bonds 1,4-di-(1-boracyclopentyl)butane is smoothly converted by ethyl

thioborate into 1-ethylthioboracyclopentane, and the latter into an ester of butane-1,4-dithioboric acid[68]:



3. Synthesis of Esters of Organothioboric Acids from Esters of Organoboric Acids

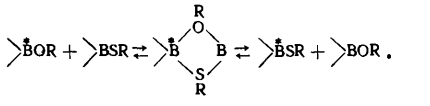
A universal and preparatively very simple method for the synthesis of esters of organothioboric acids is an exchange reaction between esters of organoboric acids and thioborates or esters of organothioboric acids.

Whereas in organoboron compounds the exchange of an alkyl radical for an alkoxy- or alkylthio-radical is effected smoothly only in the presence of compounds with B–H bonds the exchange of alkoxy- and alkylthio-groups in organic compounds of boron can be effected without a catalyst[35,36]:

$$3RB(OR')_2 + 2B(SR'')_3 \rightleftarrows 3RB(SR'')_2 + 2B(OR')_3,$$
$$3R_2BOR' + B(SR'')_3 \rightleftarrows 3R_2BSR'' + B(OR')_3,$$
$$RB(OR')_2 + R''B(SR''')_2 \rightleftarrows RB(SR''')_2 + R''B(OR')_2,$$
$$RB(OR')_2 + 2R''_2B(SR''') \rightleftarrows RB(SR''')_2 + R''_2BOR',$$
$$R_2BOR' + R''_2BSR''' \rightleftarrows R_2BSR''' + R''_2BOR'.$$

These reactions are reversible and the equilibrium can be displaced by the removal of the most volatile component in a vacuum with the reaction mass at 80–150°C. Under these conditions even after 2–3 h the equilibrium is almost completely displaced in favour of a low-boiling compound and the yields of the compounds sought is usually ◁ 90%. On using esters with radicals of different molecular weight exchange reactions of the types mentioned could be effected in any direction. This is an extremely valuable procedure for the production of esters of low molecular weight from esters of higher molecular weight. For example, with ethyl thioborate butyl propylthioborate or dibutylthioborate gave the corresponding ethyl esters in 87–97% yields.

The reaction mechanism leads to the formation of intermediate dimeric compounds and their subsequent decomposition in an energetically favourable direction:



This method of synthesis of esters of organothioboric acids was used with success for a series of alkanediboric and triboric compounds. Thus tetramethyl propane-1,3-diborate is converted into tetramethyl propane-1,3-dithioborate on heating with methyl thioborate[68]:

$$3(CH_3O)_2B(CH_2)_3B(OCH_3)_2 + 4B(SCH_3)_3 \rightarrow (CH_3S)_2B(CH_2)_3B(SCH_3)_2 + 4B(OCH_3)_3.$$

Tetraethyl butane-1,4-dithioborate was obtained from tetramethyl butane-1,4-diborate and triethylthioborate[70]:

$$3(CH_3O)_2B(CH_2)_4B(OCH_3)_2 + 4B(SC_2H_5)_3 \rightarrow$$
$$\rightarrow (C_2H_5S)_2B(CH_2)_4B(SC_2H_5)_2 + 4B(OCH_3)_3.$$

The corresponding 1,1,5,9,9-penta-alkylthio-1,5,9-triboranononanes were synthesised from 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane and trimethyl thioborate or triethyl thioborate[71]:

$$3(CH_3O)_2B(CH_2)_3\underset{\displaystyle OCH_3}{B}(CH_2)_3B(OCH_3)_2 + 5B(SR)_3 \rightarrow$$
$$\rightarrow 3(RS)_2B(CH_2)_3\underset{\displaystyle SR}{B}(CH_2)_3B(SR)_2 + 5B(OCH_3)_3$$

where R = CH_3 or C_2H_5.

When the polymers which are formed in the hydroboronation of dimethyl allylthioborate are heated with methyl thioborate in the presence of tetrapropyl diborane they give tetramethyl propane-1,3-dithioborate[72].

4. Synthesis of Esters of Organothioboric Acids from Alkylthioboranes and Unsaturated Hydrocarbons

Di(butylthio)borane reacts with hex-1-ene or oct-1-ene to form the esters of the corresponding organothioboric acids[73]:

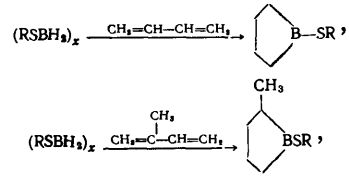
$$(n\text{-}C_4H_9S)_2BH + CH_2{=}CHR \rightarrow RCH_2CH_2B(SC_4H_{9}\text{-}n)_2.$$

The reaction with propene or 2-methylpropene is complex, leading to mixtures of butyl alkylthioborates, dialkylthioborates, and tributyl thioborate. The reaction of polymeric butylthioborane with ethylene or propene is also complex but with hex-1-ene an ester of dihexylthioboric acid is obtained in 60% yield[74]:

$$(n\text{-}C_4H_9SBH_2)_x + 2x\,CH_2{=}CHC_4H_9 \rightarrow x(C_6H_{13})_2BSC_4H_{9}\text{-}n.$$

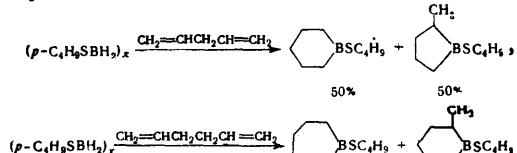
Methyl esters of diethylthioboric, dihexylthioboric, and dicyclohexylthioboric acids were obtained from methylthioborane polymer and ethylene, hex-1-ene, and cyclohexene[74].

1-Alkylthioboracycloalkanes can be synthesised from polymers of alkylthioboranes and diene hydrocarbons. Thus the reaction of polymers of methylthioborane or butylthioborane with dienes (buta-1,3-diene or isoprene) in ethereal medium gave 1-methylthioboracyclopentane[74], 1-butylthioboracyclopentane[75,76], 3-methyl-1-methylthioboracyclopentane[74], and 3-methyl-1-butylthioboracyclopentane[76]:



where R = CH_3 or n-C_4H_9.

The reaction of the polymer of butylthioborane with penta-1,4-diene or hexa-1,5-diene gives a mixture of alkylthioboracyclanes[76]:



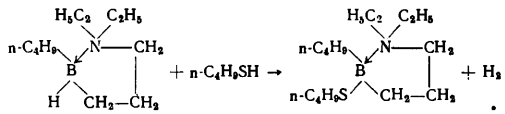
5. Synthesis of Esters of Organothioboric Acids from Alkyldiboranes or Aminoalkyl(aryl)boranes

Esters of organodialkylthioboric acids are formed by the action of thiols on tetra-alkyldiboranes[12,77]:

$$R_4B_2H_2 + 2RSH \rightarrow 2R_2BSR + 2H_2 .$$

The reactions are complicated by the formation of small amounts of side-products, owing to the symmetrisation of the initial compounds.

Butyl-(3-diethylaminopropyl)borane reacts with a thiol at 190°C to form an ester of butyl-(3-diethylaminopropyl)-thioboric acid[55]:



Esters of alkylthioboric acids are formed on heating trimethylamine–alkylboranes with thiols[17,78]:

$$RBH_2 \cdot N(CH_3)_3 + 2RSH \xrightarrow{60-100^\circ} BB(SR')_2 + 2H_2 + N(CH_3)_3 .$$

Esters of dialkylaminoarylboric acids are obtained by the action of thiols on dialkylaminoarylboranes[79].

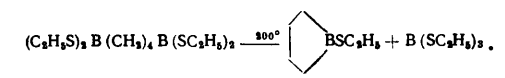
B. PROPERTIES

1. Thermal Conversions

Esters of organothioboric acids are compounds of rather high thermal stability. Thus propyl dipropylthioborate is unchanged after heating for 4 h at 160°C.[64] However, long heating at a high temperature leads to disproportionation of thioesters. After 34 days at 84°C dimethyl methylthioborate is 10% symmetrised into methylthioborate and methyl dimethylthioborate[21], and dibutyl isobutylthioborate after 10 h at 240–250°C was 30% converted into butyl thioborate and butyl di-isobutylthioborate[37]:

$$\text{iso-}C_4H_9B(SC_4H_9\text{-}n)_2 \rightleftarrows (\text{iso-}C_4H_9)_2BSC_4H_9\text{-}n + B(SC_4H_9\text{-}n)_3 .$$

On heating, esters of butane-1,4-dithioboric acid are converted into thioborate and 1-alkylthioboracyclopentane[70]:



2. Hydrolysis and Alcoholysis

Esters of organothioboric acids are readily hydrolysed by water with the formation of organoboric acids and thiols:

$$R_2BSR + H_2O \rightarrow R_2BOH + RSH .$$

Under the action of alcohols esters of organothioboric acids are also readily converted into esters of organoboric acids[64]. With alcohols, alkylthio-derivatives of boracycloalkanes give 1-alkoxyboracycloalkanes[75].

Smooth and rapid reaction of thioesters with alcohols allows esters of dialkylboric acids to be synthesised from boron trialkyls under mild conditions including the difficultly accessible methyl esters by using a catalytic quantity of thiol in the reaction[80]:

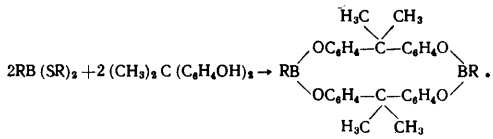
$$BR_3 + CH_3OH \xrightarrow[65-70^\circ]{RSH} R_2BOCH_3 + RH .$$

The thiol and the boron trialkyl form esters of dialkylthioboric acids and thiol, which again reacts with the boron trialkyl. In this way tris-(3-dimethoxyborylpropyl)boron is smoothly converted into 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane and dimethyl propylborate[81]:

$$B[CH_2CH_2CH_2B(OCH_3)_2]_3 + CH_3OH \xrightarrow{C_2H_5SH,\ 100^\circ} \rightarrow (CH_3O)_2B(CH_2)_3B(CH_2)_3B(OCH_3)_2 + n\text{-}C_3H_7B(OCH_3)_2 .$$

Under the action of alcohols, esters of alkylthioboric acids give dialkyl alkylborates.

Dialkyl esters of organoalkylthioboric acids and organoarylthioboric acids form heterocyclic compounds with 2,2-bis-(4-hydroxyphenyl)propane[82] [Bisphenol A]:



3. Reactions with Ammonia and Amines

Esters of dialkylthioboric acids give dialkylboramines with ammonia[63,80,83]. On introducing ammonia into a cooled ester of organothioboric acid an adduct is formed, which decomposes at ~20°C with loss of thiol into dialkylboramines with almost quantitative yield:

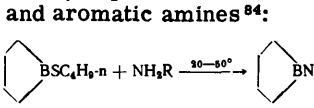
$$R_2BSR' + NH_3 \rightarrow R_2BSR' \cdot NH_3 \rightarrow R_2BNH_2 + R'SH .$$

Dialkylboramines can be obtained starting directly from boron trialkyls and ammonia by using a little thiol, which plays the part of a catalyst of the reaction[80,83]. The thioester formed in the first stage of the reaction between the boron trialkyl and the thiol reacts with the ammonia to regenerate the thiol, which again reacts with the boron trialkyls, and the process is repeated until the boron trialkyl is completely consumed. Esters of diarylthioboric acids also react smoothly in the cold with ammonia to form diarylboramines[42].

With amines the esters of dialkylthioboric acids form *N*-substituted dialkylboramines[63,64,83]:

$$R_2BSR' + NH_2R'' \rightarrow R_2BNHR'' + R'SH .$$

Just as in the synthesis of dialkylboramines, the production of their *N*-substituted derivatives is possible directly from boron trialkyls and amines in the presence of trace amounts of thiols[80,83]. Esters of diarylthioboric acids and 1-alkylthioboracyclopentane[76,85] react similarly with aliphatic[42] and aromatic amines[84]:



With hexamethylenediamine the esters of dialkylthioboric acids form *NN'*-di(dialkylboryl)-1,6-diaminohexanes:

$$2R_2BSR' + H_2N(CH_2)_6NH_2 \xrightarrow[85\%]{160-180^\circ} R_2BNH(CH_2)_6NHBR_2 + 2R'SH;$$

with hydrazine they give 1,2-bis(dialkylboryl)hydrazines

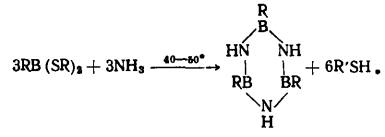
$$2R_2BSR' + NH_2-NH_2 \xrightarrow[80\%]{150-180^\circ} R_2BNH-NHBR_2 + 2R'SH;$$

and with phenylhydrazine they are converted into 2-(dialkylboryl)-1-phenylhydrazines[63]:

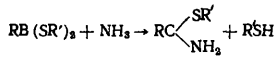
$$R_2BSR' + NH_2NHC_6H_5 \xrightarrow[70\%]{160-200^\circ} R_2BNH-NHC_6H_5 + R'SH .$$

The reactions of esters of alkylthioboric and arylthioboric acids with ammonia and amines leads to a different nitrogen-containing compound of boron.

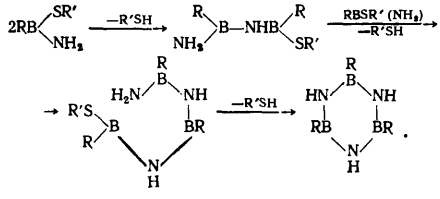
Ammonia with dialkyl esters of organothioboric acids gives *B*-trialkylborazoles smoothly[42,86]



The mechanism of the reaction leads to the formation of an amino-ester in the first stage:

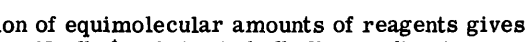


which then is apparently condensed by the following scheme:



This is an effective method for the synthesis of *B*-trisubstituted borazoles, which is also applicable for the production of *B*-triallylborazole[57].

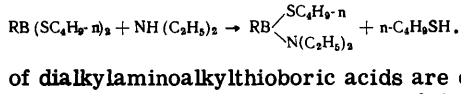
Unlike the reactions with ammonia, with 2 moles of primary aliphatic amines both alkylthio-groups in esters of alkylthioboric acids are replaced by alkylamino-groups to form *N*-alkyl-substituted alkylborondiamines[87]:



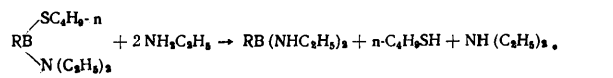
The reaction of equimolecular amounts of reagents gives a mixture of an *N*-alkyl-substituted alkylboron diamine, an aminothioester, and the initial thioester.

Diethyl allylthioborate and butylamine form allyldibutylaminoboron[57].

Esters of alkylthioboric acids behave quite differently with secondary aliphatic amines (for example, diethylamine). Here only one alkylthio-group is replaced by an alkylamino-residue with formation of esters of dialkylamino-acids[87]:



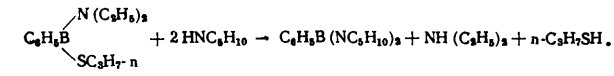
Esters of dialkylaminoalkylthioboric acids are capable of reacting with ethylamine; when an excess of the amine is used both the alkylthio- and the diethylamino-groups are replaced by the ethylamino-group and *N*-ethyl derivatives of alkylborondiamine are obtained[87]:



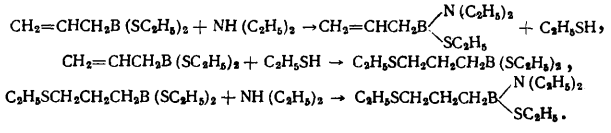
The difference in the behaviour of the esters of diethylaminoalkylthioboric acids towards ethylamine and diethylamine is evidently due to the latter's lower ability to form complexes.

Esters of dialkylaminoaryl thioboric acids behave in relation to primary amines similarly to compounds of the alkyl series, with both alkylthio- and dialkylamino-groups being replace by alkylamino-groups to form *N*-alkyl-substituted arylborondiamines[79].

The esters of dialkylaminoarylthioboric acids are more stable towards secondary amines. When a secondary amine with a high boiling point is used and the thiol and low-boiling secondary amine produced are distilled off from the reaction mass, bis(dialkylamino)arylboron can be obtained[48]:



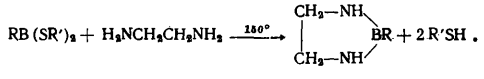
The reaction of diethyl allylthioborate with diethylamine is unique[57]. Approximately equal amounts of ethyl diethylaminoallylthioborate and ethyl diethylamino-3-ethylthiopropylthioborate are obtained. In the first stage of the reaction the ethylthio-group is replaced by diethylamino-, then the ethylthiol thus obtained adds to the initial ester and the ester of 3-ethylthiopropylthioboric acid formed exchanges an alkylthio-group for a diethylamino-group:



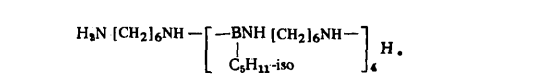
The replacement of an ethylthio-group by diethylamino- in mixed esters does not take place, as for the esters of alkylthioboric acids[87].

Dibutyl phenylthioborate and diethylamine react to form butyl diethylamino(phenyl)borate[79].

The reactions of esters of alkylthioboric acids with diamines proceed differently, depending on the nature of the latter. With ethylenediamine, 2-alkyl-1,3,2-diazoborolidines are obtained[42]:

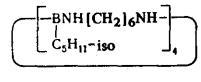


Gentle heating of dibutyl isopentylthioborate with two moles of hexamethylenediamine followed by removal of butylthiol and the unreacted diamine in a vacuum yields a benzene-soluble resinous linear polymer (I) of molecular weight 900, which includes in its structure four $RBNH[CH_2]_6NH-$ chains and an $NH_2[CH_2]_6NH$ terminal group[82]:



(I)

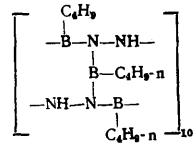
The reaction with equimolecular amounts of the reagents gives the cyclic polymer (II): structure:



(II)

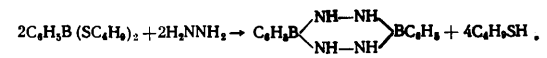
A similar polymer is obtained in the reaction of hexamethylenediamine and dibutyl butylthioborate.

With hydrazine, the esters of alkylthioboric acids give polymers[82] probably having a reticular cyclic structure (III) in which each link contains three RB< groups and two >N–NH– groups, and the number of links is shown by molecular weight determinations to be 10.

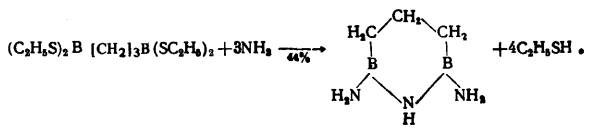


(III)

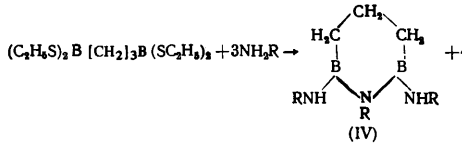
The reaction of hydrazine with an ester of phenylthioboric acid proceeds differently, leading to the formation of 3,6-diphenyl-3,6-dibora-1,2,4,5-tetrazine[82]:



The action of ammonia on tetraethyl propane-1,3-dithioborate yields 2,5-diamino-1-aza-2,5-diboracyclohexane[88]:

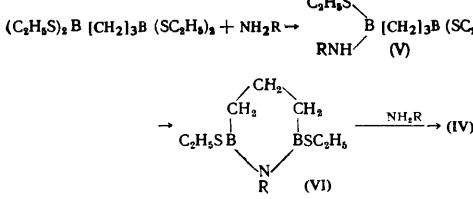


With primary amines (methylamine or ethylamine), cyclic compounds (IV) are also obtained—1-alkyl-2,5-di-(alkylamino)-1-aza-2,5-diboracyclohexanes:



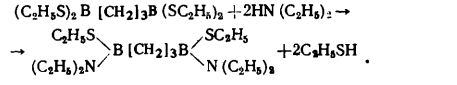
(IV)

In the first stage of the reaction one of the alkylthio-groups in the thio-ester is replaced by an alkylamino-group and the compound (V) which results is cyclised with loss of a thiol into compound (VI), which subsequently exchanges an alkylthio-group, being converted into a compound of type (IV):

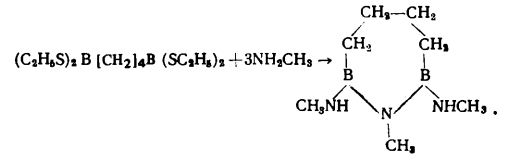


The reaction of tetraethyl propane-1,3-dithioborate with dimethylamine leads to 1,3-bis-[di(dimethylamino)bora]-propane[88].

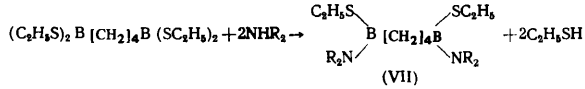
With diethylamine, esters of propane-1,3-dithioboric acid give, like esters of alkylthioboric acids, mixed (alkylamino)alkylthio-derivatives[88]:



The esters of butane-1,4-dithioboric acid react with amines similarly to the esters of propane-1,3-dithioboric acid[70]. The action of an excess of methylamine gives smoothly a seven-membered heterocyclic compound—1-methyl-2,7-bis(methylamino)-1-aza-2,7-diboracycloheptane:

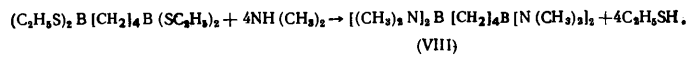


In the reaction with secondary amines the replacement of two alkylthio-groups takes place very readily with the formation of 1,4-bis(dialkylaminoethylthiobora)butane (VII)[70]:



(VII)

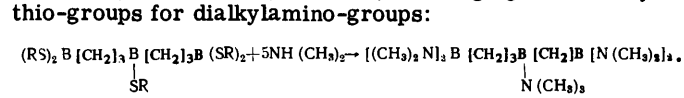
The further replacement of alkylthio-groups is effected by the use of a large excess of the dialkylamine, heating (80–100°C), and periodically distilling off in a vacuum the thiol formed in the reaction:



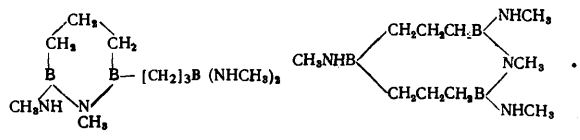
(VIII)

The reverse reaction—the replacement of the dimethylamino-group in compound (VIII) by ethylthio-groups—also proceeds with difficulty, only two of them being replaced, with formation of the compound (VII; R = CH_3).

1,1,5,9,9-Penta-alkylthio-1,5,9-triboranonanes react vigorously with dimethylamine[71], exchanging all the alkylthio-groups for dialkylamino-groups:

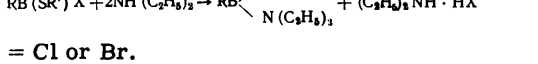


With methylamine a substance with structure (IX) or (X) is formed:



(IX) (X)

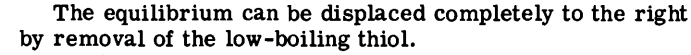
The action of diethylamine on esters of halogenoalkylthioboric acids causes halogen atom replacement by an alkylamino-group, with formation of esters of (diethylamino)alkylthioboric acids[43] resistant to further action by diethylamine:



where X = Cl or Br.

4. Reactions with Thiols, Hydrogen Sulphide, and Hydrogen Cyanide

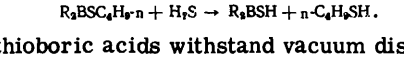
Esters of dialkylthioboric acids are readily re-esterified by higher thiols on heating[52]:



The equilibrium can be displaced completely to the right by removal of the low-boiling thiol.

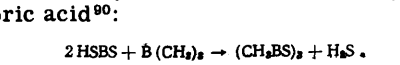
Diethyl allylthioborate adds ethanethiol to form an ester of 3-ethylthiopropylthioborate[56,57].

When treated with hydrogen sulphide and heated to 140–180°C esters of organodialkylthioboric acids form dialkylthioboric acids and a thiol[89]:



Organothioboric acids withstand vacuum distillation. Prolonged heating of dibutylthioboric acid at 180–250°C decomposes it into hydrogen sulphide, hydrogen, butene, butane, and uninvestigated sulphur-containing organoboron compounds.

The reaction of esters of organoalkylthioboric acids with hydrogen sulphide, as a result of which anhydrides of alkylthioboric acids could be obtained, has not been investigated. One of the representatives of this class of compound—the trimer of the anhydride of methylthioboric acid—was obtained by the reaction of trimethylboron and metathioboric acid[90]:



The trimer is stable only in the solid state; in solutions a greater association of the anhydride is observed.

In solution the polymeric anhydride of metathioboric acid is oxidised by oxygen into $(CH_3OBS)_3$,[90] which can also be obtained by the action of trimethyl borate on metathioboric acid[31] or $(BrBS)_3$:[91]

$$(HSBS)_3 \xrightarrow[-B(SH)_3]{B(OCH_3)_3} (CH_3OBS)_3 \xleftarrow[-BBr_3]{B(OCH_3)_3} (BrBS)_3 .$$

Butyl dialkylthioborates react with hydrogen cyanide in the cold or on gentle heating to form dialkylcyanoborons[89]:

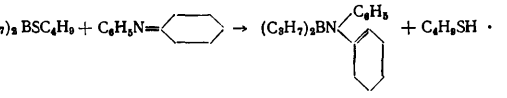
$$R_2BSC_4H_9\text{-}n + HCN \rightarrow [R_2BSC_4H_9\text{-}n \cdot HCN] \rightarrow R_2BCN + n\text{-}C_4H_9SH .$$

5. Reactions with Vinyl Esters, Cyclohexylideneaniline, and Nitriles

Esters of dialkylthioboric acids are capable of reacting with various classes of unsaturated organic compounds. Like thioborates they react with alkyl vinyl ethers, as a result of which alkyl vinyl sulphides and esters of dialkylboric acids are formed[39]. Evidently, as for thioborates the process proceeds by addition of the thioester at the multiple bond followed by β decomposition:

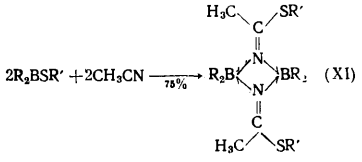
$$R_2BSC_4H_9 + CH_2=CHOC_4H_9 \rightarrow \left[R_2BCH_2CH\begin{matrix}OR\\SC_4H_9\end{matrix}\right] \rightarrow CH_2=CHSC_4H_9 + R_2BOR.$$

On heating an ester of dipropylthioboric acid with cyclohexanone anil, (cyclohexenylyl)phenylaminodipropylboron and a thiol are formed[39]:



Evidently the anil reacts in the tautomeric form as an enamine.

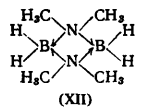
Esters of dialkyl and diaryl-thioboric acids are capable of adding at room temperature to acetonitrile with formation of 1,3-di-(1-alkylthioethylidene)-2,2,4,4-tetra-alkylcyclodiborazones (XI):[92]



where R′ = C_2H_5, or n-C_4H_9.

Infrared spectroscopy showed that in the first stage of the reaction the addition product $R_2BN{=}CCH_3(SR)$ is formed, which then dimerises into compound (XI). This is unchanged in air and is not decomposed at room temperature by alcohol, water, or even hydrochloric acid.

Concerning the nature of the chemical bond in derivatives of cyclodiborazane (XI), in these compounds, as in the dimers of aminoboranes (cyclodiborazanes), the trimers of aminoboranes (cyclotriborazanes), and other such compounds (trimers of phosphinoboranes, alkylthioboranes), all the bonds of the boron atom with a heteroatom (N, P, S) are equivalent. The equivalence of the chemical bonds in this type of compound, for example, in 1,1,3,3-tetramethylcyclodiborazane (XII)



(XII)

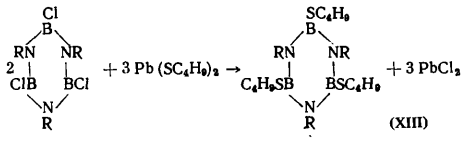
is attained by the formation of a special type of coordinate bond between the boron atom and the heteroatom. In this coordination interaction, each boron atom allows one tetrahedral orbital (sp^3) and one electron for covalent bonds with hydrogen atoms and one sp^3-orbital and $\frac{1}{2}$ electron for bonds with each neighbouring nitrogen atom. On the other hand, each nitrogen atom supplies an sp^3-orbital and one electron for its bonds with each carbon atom and one sp^3-orbital and 1.5 electrons for bonds with each neighbouring boron atom. It is desirable to call this type of bond semicoordinate and to represent it with a half-arrow.

In cyclodiborazanes of type (XI) the bond between the boron and nitrogen atoms also has a semicoordinate nature, the only difference being that each nitrogen atom in a $tr^2trtr\pi$ valence state provides for the double bond with the carbon atom one trigonal orbital (sp^2, or in another notation tr) and one π orbital whereas for the bond with each neighbouring boron atom one trigonal orbital (tr). The semicoordinate bonds formed by the trigonal orbitals of the nitrogen atom are stronger than those with tetrahedral orbitals.

IV. *B*-ALKYLTHIOBORAZOLES

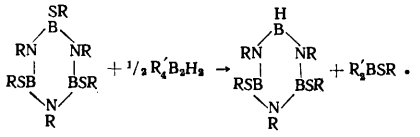
A. METHODS OF PRODUCTION

B-Trialkylthioborazoles (XIII) were synthesised by heating *B*-trichloroborazoles with lead mercaptides in benzene, the yields being 70–90%:[93]



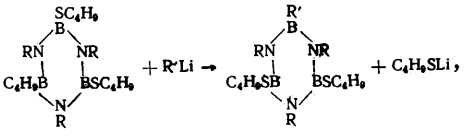
where R = H, CH_3, C_2H_5.

B-Trialkylthioborazoles served as starting materials for the synthesis of unsymmetrical *B*-dialkylthioborazoles. The latter were obtained by heating *B*-trialkylthioborazoles with tetrapropyldiborane[94]:



B-Dialkylthio-derivatives of borazole can also be obtained by the action of tetra-alkyldiborane on *B*-trichloroborazoles with subsequent treatment of the reaction products with lead mercaptide.

In the reaction of organomagnesium compounds with *B*-trialkylthioborazoles small yields of *B*-alkyl-*B*-dialkylthioborazoles are obtained[95]. With organolithium compounds the stepwise replacement of alkylthio-groups by alkyl radicals proceeds more smoothly and from *B*-trialkylthio-*N*-trialkylborazoles it was possible to obtain by this method *B*-alkyl-*B*-dialkylthio-*N*-trialkylborazoles in 62–65% yields:



where R = CH_3, C_2H_5, R′ = C_2H_5, n-C_4H_9.

B. PROPERTIES

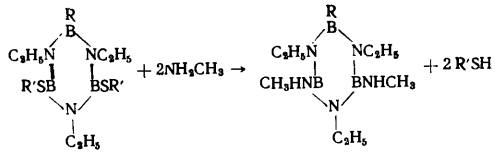
B-Trialkylthioborazoles are, like esters of organothioboric acids, highly reactive. With alcohols they exchange alkylthio-groups for alkoxyl groups in the cold to give *B*-trialkoxyborazoles.[95]

B-Tributylthioborazoles react in the cold with primary or secondary amines, forming the corresponding *B*-alkylamino-derivatives[93]. Thus *B*-tributylthioborazole and dimethylamine gave *B*-tri(dimethylamino)borazole (yield 97%) and the action of aniline on *B*-tributylthioborazole or *B*-tributylthio-*N*-triethylborazole gave respectively *B*-triphenylaminoborazole and *B*-triphenylamino-*N*-triethylborazole.

On introducing ammonia into a benzene solution of *B*-trialkylthioborazoles, *B*-triamino-substituted borazoles are obtained[93]. Like the esters of organothioboric acids, *B*-trialkylthioborazoles are capable of re-esterification on heating with higher thiols[96].

The synthesis of various unsymmetric derivatives of borazole has been effected from *B*-alkyl-*B*-dialkylthio-*N*-trialkylborazoles[95]. *B*-Butyl-*B*-dimethoxy-*N*-triethylborazole was obtained by treatment of *B*-butyl-*B*-dibutylthio-*N*-triethylborazole with methanol.

The reactions with primary or secondary amines take place with high yields:

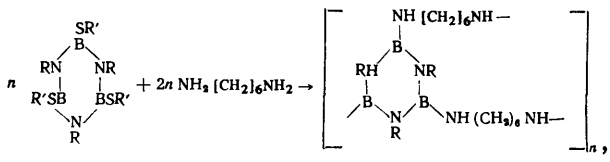


where R = C_2H_5, n-C_4H_9, R′ = n-C_4H_9.

B-Dialkylthio-*N*-trialkylborazoles undergo analogous exchange reactions with amines[96].

Starting from *B*-alkylthio-derivatives of borazole, three-dimensional and linear polymers can be obtained[97]. Polycondensation with participation of *B*-alkylthio-derivatives of borazole takes place under mild conditions ensuring retention of the borazole ring and the regularity of the repeating units.

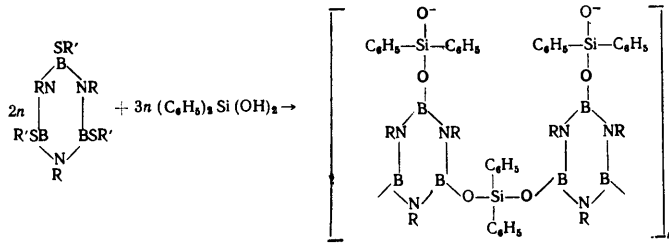
The condensation of the *B*-tributylthio-*N*-trialkylborazoles with hexamethylenediamine in *o*-xylene at 125°C gave polymers (XIV) which were thermostable powders, insoluble in ordinary organic solvents, hydrolysing in air:



(XIV)

where R = CH_3, C_2H_5.

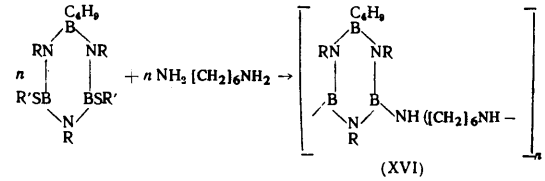
B-Tributylthio-*N*-trimethylborazole with diphenylsilandiol (1 : 1.5) in ethereal medium gives a powdered thermostable polymer (XV) not hydrolysed in air, soluble in tetrahydrofuran or dioxan:



(XV)

where R = CH_3.

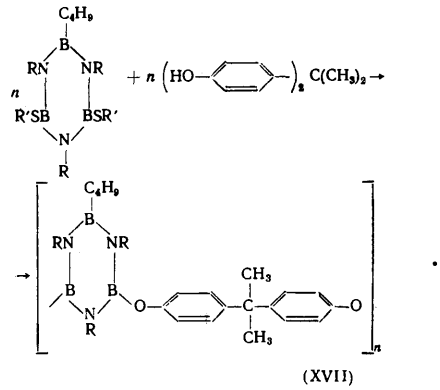
The condensation of *B*-butyl-*B*-dibutylthio-*N*-trialkylborazoles with hexamethylenediamine (1 : 1) in benzene gave linear polymers (XVI) which are brittle substances, less hydrolysed in air than three-dimensional polymers and more stable thermally (decomposition temperature > 400°C)[97]:



(XVI)

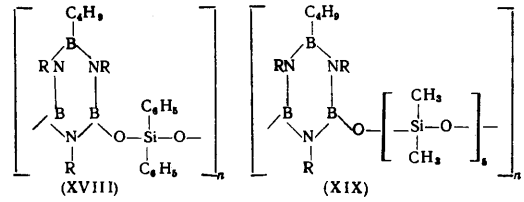
where R = CH_3, C_2H_5.

Linear polymers from *B*-butyl-*B*-dibutylthio-*N*-trialkylborazoles and 2,2-bis-(4-hydroxyphenyl)propane (XVII) are comparatively low-melting but more resistant to hydrolysis than polymers from hexamethylenediamine:



(XVII)

The reaction of *B*-butyl-*B*-dibutylthio-*N*-trimethylborazole and diphenylsilandiol[97] in boiling ethereal solution gives a viscous liquid of molecular weight ~ 1200, which corresponds with a cyclic trimer (XVIII; $n = 3$). Heating in a vacuum at 200°C converts the trimer into a brittle solid polymer (XVIII):



(XVIII) (XIX)

The condensation of *B*-butyl-*B*-dibutylthio-*N*-trimethylborazole with decamethyl-1,9-dihydroxypentasiloxane[97] in ethereal solution leads to a liquid with molecular weight ~ 1100, evidently possessing a cyclic structure (XIX; $n = 2$). On heating in a vacuum the dimer is converted into an elastic polymer (XIX) m.p. 146–149°C, which is not hydrolysed in air.

V. 1,2-THIABOROLANES

A. METHODS OF PREPARATION

1,2-Thiaborolanes are obtained by the addition of 1,2-dialkyl or 1,2-diaryl diboranes to allylthiol[98,99]:

$$^1/_2(RBH_2)_2 + CH_2{=}CHCH_2SH \rightarrow RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + H_2 ,$$

where R = n-C_4H_9, iso-C_4H_9, or C_6H_5.

2-Alkyl-1,2-thiaborolanes can be synthesised by heating mixtures of a boron trialkyl, trialkylamine–borane, and allenethiol[98]:

$$R_3B + 2\,H_3B\cdot N(C_2H_5)_3 + 3\,CH_2{=}CHCH_2SH \xrightarrow{110^\circ} 3\,RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix}.$$

B. PROPERTIES

Unlike the 2-alkyl-1,2-azaborolidines, which tend to dimerise[100], 1,2-thiaborolanes exist in a monomeric form. A feature of the cyclic structure of the 1,2-thiaborolanes appears in the definite ability to form complexes with amines which sharply distinguishes them from the related esters of dialkylthioboric acids R_2BSR.

An increase in the complex-forming ability of 1,2-thiaborolanes (and other such compounds: 1,2-azaborolidines, 1,2-oxaborolanes) is explained by the smaller reorganisation energy of the molecule compared with the acyclic compounds, when the boron atom changes from a trigonal to a tetrahedral valence state. The losses in reorganisation energy add up to the difference between the promotion energies of the boron atom from the ground state into tetrahedral and trigonal, 2.1 eV [101] and the decrease in the boron–element (C, S, N, O) bonds with decrease in the *s*-character of the boron orbitals.

In cyclic boron compounds, in which the angle of the C–B–X bonds in the ring (X = C, S, N, O) approaches the tetrahedral angle, during complex formation there is a weakening of only one (acyclic) boron–element bond, and not three, as occurs in compounds of the type BX_3, which is due to a decrease in the reorganisation energy. Strictly speaking, the energy of the outer B–X bond in the cyclic compound decreases to a larger extent in complex formation than in the compounds of the type BX_3, so that the *s*-character of the boron orbitals in this bond is greater than 0.33, but evidently the energetic losses occurring during this are less than in the change of two B_{tr}–X bonds into B_{te}–X bonds. The gain in reorganisation energy during complex formation in cyclic boron compounds in comparison with the acyclic analogues is adequate equal to more than adequate to compensate for the strain energy in the ring.

2-Butyl-1,2-thiaborolane forms a stable liquid complex with pyridine capable vacuum distillation without decomposition. Like other coordination compounds of boron this complex has a high dipole moment (5.2 D), whereas the dipole moment of the original thiaborolane is only 1.5 D.

Alkylthiaborolanes also form stable complexes with secondary and primary amines or ammonia (XX) which distil in vacuum without decomposition:

$$RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + L \rightarrow \begin{matrix}R\\ L\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} \quad (XX)$$

where R = n-C_4H_9, iso-C_4H_9; L = NH_3, $NH_2C_2H_5$, $NH(C_2H_5)_2$, NHn-C_4H_9, $NH(n\text{-}C_4H_9)_2$, HNC_5H_{10}.

In the infrared spectra of the compounds (XX; L = NHR_2) there are absorption bands in the region 3050–3300 cm^{-1} corresponding to the stretching vibrations of the N–H bonds and the absence of S–H bands. In the infrared spectrum of the compound (XX; L = NH_2R) there is an intense band with a maximum at 1582 cm^{-1} due to the deformation vibrations of the NH_2 groups.

Less stable complexes are given by alkylthiaborolanes with sterically hindered amines. Thus 2-butyl-1,5-thiaborolane forms a complex, with evolution of heat, with t-butylamine; however, on heating, the complex decomposes into the initial substances.

Unlike the primary and secondary amines, when alcohols act on 2-alkyl-1,2-thiaborolanes there is breaking of the B–S bond with formation of esters of (3-mercaptopropyl)alkylboric acids (XXI):

$$RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + R'OH \rightarrow \begin{matrix}R\\ R'O\end{matrix}\!\!>\!B{-}CH_2CH_2CH_2SH . \quad (XXI)$$

2-Butylthiaborolane reacts with 2-aminoethanol similarly to give crystalline 2-aminoethyl (3-mercaptopropyl)-butylborate:

$$n\text{-}C_4H_9B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + HOCH_2CH_2NH_2 \rightarrow \begin{matrix}n\text{-}C_4H_9\\ HSCH_2CH_2CH_2\end{matrix}\!\!>\!B\begin{matrix}NH_2{-}CH_2\\ |\\ O{-}CH_2\end{matrix}.$$

The infrared spectra of compounds (XXI) have an absorption band in the 2580 cm^{-1} range (S–H); there is also strong absorption in the range for the B–O bond but OH absorption is absent. The fact that this reaction does not stop at the complex formation stage and nucleophilic substitution occurs at the boron atom can be explained by the weaker complex-forming ability of alcohols in comparison with amines and the higher energy of the B–O bond in comparison with the B–N bond.

In the reaction of butanol with the pyridine complex of 2-butyl-1,2-thiaborolane breaking of the B–S bond also occurs and pyridine and butyl (3-mercaptopropyl)butylborate are formed:

$$\begin{matrix}n\text{-}C_4H_9\\ C_5H_5N\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + n\text{-}C_4H_9OH \rightarrow \begin{matrix}n\text{-}C_4H_9\\ n\text{-}C_4H_9O\end{matrix}\!\!>\!B{-}CH_2CH_2CH_2SH + C_5H_5N.$$

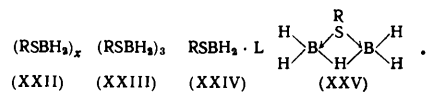
With piperidine the latter loses a molecule of alcohol, forming a piperidine complex of alkylthiaborolane:

$$\begin{matrix}n\text{-}C_4H_9\\ n\text{-}C_4H_9O\end{matrix}\!\!>\!BCH_2CH_2CH_2SH + C_5H_{11}N \rightarrow \begin{matrix}n\text{-}C_4H_9\\ C_5H_{11}N\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + n\text{-}C_4H_9OH.$$

VI. ALKYLTHIOBORANES

Various types of compound with alkylthio-groups and hydrogen atoms at the boron atom are known. These compounds, which differ in structure and properties, are classified together under the common name of "alkylthioboranes", since they contain the groupings $RSBH_2$ and

$(RS)_2BH$, with different modes of mutual coordination. Alkylthioboranes $RSBH_2$ are unknown in the monomeric form. They exist in the form of polymers (XXII), trimers (XXIII), and complexes with secondary or tertiary amines (XXIV):

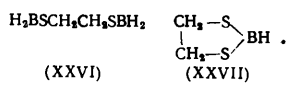


(XXII) (XXIII) (XXIV) (XXV)

A single representative of a fourth type of compound with an $RSBH_2$ grouping has been described, formed by coordination of methylthioborane with borane (XXV).

Of the $(RS)_2BH$ type of compounds di-t-butylthioborane, which exists in monomeric form, is stable. Other known dialkylthioboranes are associated to a certain extent and show a significant tendency to disproportionation.

1,2-Di(borylthio)ethane (XXVI) and 1,3,2-dithiaborolane (XXVII) have been obtained in associated form:



(XXVI) (XXVII)

1. Methods of Preparation

The reaction between diborane and thiols was first investigated by Burg and Wagner[12] for the example of methanethiol. On mixing the reagents at −78°C and holding the reaction mixture at that temperature for a few days a solid polymer of methylthioborane was obtained:

$$x/2\ B_2H_6 + x\ CH_3SH \rightarrow (CH_3S\ B\ H_2)_x + x\ H_2\ .$$

Treatment of the partly depolymerised reaction product with trimethylamine led to trimethylamine–methyl thioborane, $CH_3SBH_2.N(CH_3)_3$.

The action of diborane on a polymer of methylthioborane or trimethylamine–methylthioborane gave the thermally unstable methylthiodiborane, which rapidly decomposes at room temperature into diborane and the polymer $(CH_3SBH_2)_x$:

$$(CH_3SBH_2)_x + x/2\ B_2H_6 \rightarrow x\ CH_3SB_2H_5\ ,$$
$$CH_3SBH_2 \cdot N(CH_3)_3 + B_2H_6 \rightarrow CH_3SB_2H_5 + H_3B \cdot N(CH_3)_3 .$$

Subsequently the reactions between diborane and thiols were carried out in ethereal medium using the ordinary laboratory techniques, which allowed experiments to be performed on a large scale and the properties of the compounds thus formed to be widely investigated.

On introducing 1 mole diborane into an ethereal solution of 2 moles thiol a steady evolution of hydrogen was observed. After the reaction had ceased and the solvent had been removed in a vacuum the residue contained a solid polymer (when methanethiol or 2-methylpropane-2-thiol were used) or a syrupy product (for ethanethiol, propane-1-thiol, or butane-1-thiol)[14,102]:

$$x/2\ B_2H_6 + x\ RSH \rightarrow (RSBH_2)_x + x\ H_2\ .$$

The polymers of ethyl-, propyl-, and butyl-thioborane are converted on standing into trimers of alkylthioboranes (1,3,5-trialkylcyclotriborathianes); the polymers of methyl- and t-butyl-thioboranes are converted into trimers in tetrahydrofuran solution[14,102]:

$$(RSBH_2)_x \rightarrow x/3\ (RSBH_2)_3\ .$$

The trimers of alkylthioboranes, with the exception of the trimer of t-butyl thioborane (m.p. 105–107°C) are liquids which distil without decomposition in a vacuum.

When pentane-1-thiol, phenylmethanethiol, or thiophenol react with diborane (2 : 1) in tetrahydrofuran or Diglyme 2 moles hydrogen are rapidly liberated. The RS-substituted boranes thus formed are not isolated from the solutions and are identified solely by their infrared and NMR spectra[103,104].

Polymeric 1,2-di(borylthio)ethane is obtained from diborane and 1,2-dithioethyleneglycol[105]:

$$B_2H_6 + HSCH_2CH_2SH \rightarrow H_2BSCH_2CH_2SBH_2 + 2\ H_2\ .$$

Dipropylthioborane and dibutylthioborane are obtained by passing diborane into ethereal solutions of the corresponding thiols (1 : 4) and subsequent distillation of the reaction products[15,16]:

$$B_2H_6 + 4\ RSH \rightarrow 2\ (RSH)_2BH + 2\ H_2\ .$$

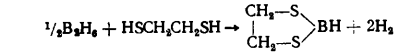
The general method for obtaining dialkylthioboranes is the reduction of alkylthioborates with lithium tetrahydroaluminate in ethereal medium[106]:

$$4\ B\ (SR)_3 + LiAlH_4 \rightarrow 4\ (RS)_2BH + LiSR + 2\ Al(SR)_3\ .$$

Dialkylthioboranes can be obtained from the trimers of alkylthioboranes and thioborates in the distillation of mixtures of these substances in the ratio 1 : 3.

$$(RSBH_2)_3 + 3\ (RS)_3B \rightarrow 6\ (RS)_2BH\ .$$

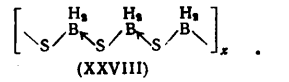
The synthesis of di-t-dodecylthioborane from aminoborane and t-dodecanethiol[49] has also been described[49]. Associated 1,3,2-dithiaborolane is obtained by the reaction of diborane and dithioethylene glycol[105]:



In the reaction of diborane and triphenylthioborate (1 : 4) in tetrahydrofuran, diphenylthioborane is formed[104], which was not isolated in a pure state and was identified solely by its NMR spectrum (doublet at −24 p.p.m., J = 140 Hz).

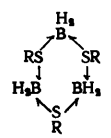
2. Physical Properties

The polymers of the alkylthioboranes are solids or syrupy substances and most of them swell in ether, are insoluble in benzene, but soluble in tetrahydrofuran. The association of the molecules of alkylthioboranes is effected by donor–acceptor bonds between the boron and sulphur atoms (XXVIII):



(XXVIII)

The trimers of alkylthioboranes are liquids with a cyclic structure (XXIX) with semicoordinate bonds between the boron and sulphur atoms, similar to the semicoordinate B–N bonds (see p. 944).



(XXIX)

The dipole moment of 1,3,5-triethylcyclotriborathiane is 2.90 D, and that of 1,3,5-tributylcyclotriborathiane, 3.16 D.

The infrared spectra of 1,3,5-trialkylcyclotriborathianes have two intense absorption bands in the range 2412–2420 cm^{-1} and 2465–2470 cm^{-1}, corresponding to the stretching vibrations of the B–H bonds.

In the ^{11}B NMR spectra of 1,3,5-triethylcyclotriborathiane at 25°C there is a broad peak (chemical shift +31 p.p.m. relative to trimethyl borate). At 90°C the broad peak is converted into a triplet with a 1 : 2 : 1 ratio of intensities[107].

In the proton magnetic resonance spectrum of 1,3,5-trimethyl cyclotriborathiane (internal standard tetramethylsilane, $\delta = 0$) there is a singlet from the protons of the methyl groups at $\delta = 2.14 \pm 0.03$ p.p.m. and a quadruplet from the protons connected with the boron, centred at $\delta = 2.35 \pm 0.02$ p.p.m., $J_{BH} = 115 \pm 5$ Hz.

The properties of the dialkylthioboranes are determined by the nature of the alkyl groups. The infrared spectrum of monomeric di-t-butylthioborane has an absorption band at 2545 cm^{-1} corresponding to the B–H stretching vibrations. The ^{11}B NMR spectrum at room temperature is a weakly resolved doublet with chemical shift −40.7 p.p.m. relative to $B(OCH_3)_3$. Other dialkylthioboranes tend to disproportionate and even in freshly distilled specimens the presence of ~ 20% thioborate and alkylthioboranes of a different degree of association is observed spectroscopically. During the disproportionation of the methyl and ethyl derivatives equilibrium is reached when the mixture contains ~ 20% dialkylthioborane:

$$2(RS)_2BH \rightleftarrows (RS)_3B + RSBH_2 .$$

On standing, di-isopropylthio- and dibutylthio-boranes are completely symmetrised[108]. 1,3,2-Dithiaborolane exists in the gas phase as a monomer[105]. The frequency of the B–H vibrations drops from 2595 cm^{-1} in the vapour to 2435 cm^{-1} in the solid state.

3. Chemical Properties

a. Thermal Changes. Most of the known polymers of the alkylthioboranes are slowly and spontaneously converted into trimers at room temperature[14,102]. The solid polymers of methylthioborane and t-butylthioborane are exceptions; they are converted into trimers on dissolution in tetrahydrofuran.

The trimers of alkylthioboranes (1,3,5-trialkylcyclotroborathianes) are more stable thermally and can be distilled in a vacuum, with the exception of the trimer of n-butylthioborane, which undergoes partial decomposition on distillation. Other trimers also decompose above 100°C. Thus the trimer of ethylthioborane distils from a small fractionating column without decomposition but in distillation with an efficient column the trimer decomposes, the products obtained being readily volatile substances and a very viscous distillate which ultimate analysis shows to have the composition $[(C_2H_5S)_3B_2H_3]_x$.

The results[107] suggesting that the polymeric product of composition $[(C_2H_5S)_3B_2H_3]_x$ is formed in the reaction of diborane with ethanethiol in the ratio 1 : 3 is erroneous. In reality at this ratio the reagents replace two of the hydrogen atoms in BH_3 by ethylthio-groups to only a slight extent and on distillation of the reaction products the trimer of ethylthioborane $(C_2H_5SBH)_3$ is obtained in high yield (up to 80%)[108].

b. Oxidation and Protonolysis. The trimers of the alkylthioboranes (1,3,5-trialkylcyclotriborathianes) are stable in relation to oxidants. They are almost unchanged in air and are completely unoxidised even on boiling with hydrogen peroxide in alkaline solution[14].

The polymers and trimers of the alkylthioboranes exhibit different stability towards hydrolysis. The polymers are readily hydrolysed at room temperature, whereas the trimers are only slowly hydrolysed on heating in water.

With alcohols the polymers of the alkylthioboranes readily react in the cold; alcoholysis of the trimers at room temperature proceeds very slowly, but on boiling with the alcohols they are completely decomposed, being converted into the corresponding borates, with liberation of hydrogen[14]:

$$(RSBH_2)_3 + 9\,R'OH \rightarrow 3\,B(OR')_3 + 6\,H_2 + 3\,RSH .$$

With thiols the trimers react at 100–120°C to form alkyl thioborates[14]:

$$(RSBH_2)_3 + 6\,RSH \rightarrow 3\,B(SR)_3 + 6\,H_2 .$$

Dialkylthioboranes are quantitatively hydrolysed by water in the cold to boric acid; with alcohols they give alkyl borates. The replacement of hydrogen by the alkylthio-group in dialkylthioboranes starts only at 50–60°C and proceeds rather vigorously at ~ 100°C.[15,16]

c. Reactions with amines. The trimers of the alkylthioboranes react at room temperature with secondary and tertiary amines. The reactions take place with breaking of the ring and lead to the formation of amine complexes of alkylthioboranes[109,110]:

$$(RSBH_2)_3 + 3\,R'_2R''N \rightarrow 3\,RSBH_2 \cdot NR'_2R'' ,$$

where R″ = H or alkyl.

The polymers of alkylthioboranes also give aminoalkylthioboranes with amines.

Amine complexes of the alkylthioboranes are formed by the reaction of diborane with aliphatic sulphenylamines[111]:

$$^1/_2\,B_2H_6 + CH_3SNR_2 \rightarrow CH_3SNR_2 \cdot BH_3 \rightarrow CH_3SBH_2 \cdot NHR_2 .$$

The complexes of the alkylthioboranes with tertiary amines are non-associated liquids, stable at room temperature but partly decomposing on heating[110].

The complexes of the alkylthioboranes with secondary amines undergo further changes on heating with formation both of products of the replacement of the alkylthio-groups (dialkylaminoboranes) and products with replacement of hydrogen—dialkylamino(alkylthio)boranes[110,111]:

$$RSBH_2 \cdot NHR'_2 \rightarrow \begin{cases} \rightarrow R'_2NBH_2 + RSH \\ \rightarrow R'_2N\diagdown\!\!\diagup BH + H_2 \end{cases} .$$

The reactions of amine complexes of alkylthioboranes with hydrogen chloride and with halogen derivatives of hydrocarbons have been studied[109,112]. The complexes of alkylthioboranes with dimethylamine are converted into the corresponding boronium salts with these reagents:

$$2\,RSBH_2 \cdot NH(CH_3)_2 + HCl \rightarrow \{H_2B[NH(CH_3)_2]_2\}Cl + 1/3\,(RSBH_2)_3 + RSH$$
$$2\,RSBH_2 \cdot NH(CH_3)_2 + R'X \rightarrow \{H_2B[NH(CH_3)_2]_2\}X + 1/3(RSBH_2)_3 + RSR .$$

Trialkylamine–alkylthioboranes are split by hydrogen chloride, regenerating the orginal trimer. They undergo exchange reactions with the halogen derivatives of hydrocarbons, as a result of which amine complexes of halogenoboranes and dialkyl sulphides are obtained:

$$RSBH_2 \cdot NR'_3 + R''X \rightarrow XBH_2 \cdot NR'_3 + RSR'' .$$

The complexes of alkylthioboranes with pyridine behave uniquely in relation to the halogen derivatives of hydrocarbons. With carbon tetrachloride they are converted into bis(pyridine)boronium chloride:

$$RSBH_2 \cdot NC_5H_5 + CCl_4 \rightarrow [H_2B(NC_5H_5)_2]Cl$$

and with alkyl halides they exchange an alkylthio-group for halogen:

$$RSBH_2 \cdot NC_5H_5 + R'X \rightarrow XBH_2 \cdot NC_5H_5 + RSR' .$$

There is a very interesting reaction between dimethylamine–ethylthioborane and dimethylammonium chloride, leading to the formation of bis(dimethylamino)boronium chloride:

$$RSBH_2 \cdot NH(CH_3)_2 + (CH_3)_2NH_2Cl \rightarrow \{H_2B[NH(CH_3)_2]_2\}Cl + RSH .$$

1,3,5-trialkylcyclotriborathiane also reacts readily with primary amines but the reaction is different from that with secondary and tertiary amines[113]. When methylamine or ethylamine react with the trimers of the alkylthioboranes, irrespective of the ratio of the reagents, boronium salts are obtained–mercaptides of bis(methylamino)boronium or bis(ethylamino)boronium, respectively:

$$(RSBH_2)_3 + 6\,R'NH_2 \rightarrow 3\,[H_2B(NH_2R')_2]SR .$$

The mercaptide ion of bis(alkylamino)boronium mercaptides is replaced by the chloride ion when they are treated with an ethereal solution of hydrogen chloride:

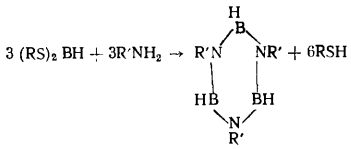
$$[H_2B(NH_2R')_2SR + HCl \rightarrow [H_2B(NH_2R')_2]Cl + RSH .$$

A similar exchange takes place on reaction with benzyl chloride.

Bis(alkylamino)boronium chlorides can be obtained directly from the trimers of alkylthioboranes with primary amines in the presence of benzyl chloride:

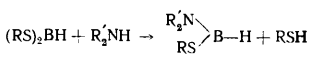
$$(RSBH_2)_3 + 6\,NH_2R' + 3\,C_6H_5CH_2Cl \rightarrow 3\,[H_2B(NH_2R')_2]Cl + 3\,C_6H_5CH_2SR .$$

Dialkylthioboranes react with amines at room temperature. With primary amines, dialkylthioboranes give *N*-trialkylborazoles[16]:



where R′ = C_2H_5, n-C_4H_9.

With secondary amines, depending on the nature of the reagents dialkylamino(alkylthio)boranes RS(R_2N)BH or bis(dialkylamino)boranes are obtained[114]:



$$(RS)_2BH + 2R'_2NH \rightarrow (R'_2N)_2BH + 2RSH .$$

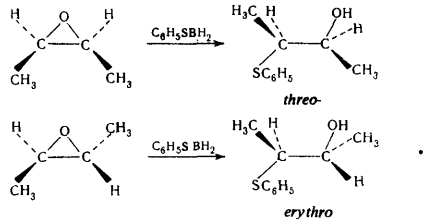
The reactions of dialkylthioboranes with tertiary amines lead to the formation of $(RS)_2BH$.amine complexes. 1,3,2-Dithiaborolane forms complexes with trimethylamine and trimethylphosphine[105].

d. Reactions with Ethers, Oxides, and Carbonyl Compounds. Phenylthioborane, pentylthioborane, and benzylthioborane are split into ethers at room temperature[103,104]:

$$RSBH_2 + R'{-}O{-}R' \rightarrow RSR + H_2BOR'' .$$

For example, in 1,2-dimethoxyethane at 25°C phenylthioborane is 79% converted after 20 h into thioanisole, and in tetrahydrofuran it gives 4-(phenylthio)butan-1-ol in 45% yield after 3 h.

Oxides of unsaturated hydrocarbons react with phenylthioborane and alkylthioboranes (pentylthio- and benzylthio-derivatives) with breaking of the oxide ring[104,115] The stereochemical direction of these reactions depends on the nature of the oxides[115]. In the reaction of phenylthioborane with *cis*- and *trans*-2,3-epoxybutane trans-opening of the epoxide ring occurs, since as a result only the *threo*- and only the *erythro*-3-phenylthiobutan-2-ols respectively are formed:



The reaction of phenylthioborane with cyclohexene is just as selective, leading to the trans-2-phenylthiocyclohexanol. The stereochemical course of these reactions is inconsistent both with a four-centre mechanism[103] and a mechanism with participation of carbonium ion intermediates. The mechanism of the trans-opening of the oxide ring in this reaction remains uncertain.

The reaction of phenylthiol with *trans*-αα′-epoxybibenzyl is complicated, and with diglyme as a solvent only 6% *threo*- and 6%-*erythro*-1,2-diphenyl-2-phenylthioethanol are obtained, the main product (45%) being 1,2-diphenylethanol.

Phenylthioboranes obtained from thiophenol and diborane in tetrahydrofuran, react with optically active L-(−)-styrene oxide with the formation of only L-(−)-2-phenyl-2-phenylthioethanol.

Phenylthioborane reduces carbonyl compounds and acids (benzaldehyde, acetophenone, benzoic acid, ethyl benzoate) in alcohols but does not react with benzyl chloride[104].

d. Reactions with alkenes. The polymers of alkylthioboranes react with alkenes in ethereal medium, and the course of the process depends on the nature of the reagents[74]. A polymer of methylthioborane in the form of a gelatinous mass containing only a little solid polymer adds to ethylene, hex-1-ene, or cyclohexene with gentle heating (1.5 h at 50°C) with the formation of the corresponding esters of dialkylthioboric acids:

$$(CH_3SBH_2)_x + \text{olefin} \rightarrow R_2BSCH_3 .$$

The hydroboronation of ethylene or propene by the polymer of butylthioborane is accompanied by symmetrisation in which, as well as the butyl dialkylborate, appreciable amounts of borontrialkyl and dibutylthioborane are obtained. The reaction with hex-1-ene is smoother, leading to a satisfactory yield of an ester of dihexylthioboric acid.

In the hydroboronation of hex-1-ene by phenylthioborane in tetrahydrofuran solution (25°C, 1–1.5 h) and subsequent methanolysis of the reaction products methyl dihexylborate (45%) and dimethyl hexylborate (21%) are formed. The reaction of phenylthioborane with styrene is similar. Oxidation of the hydroboronation products gives 2-phenylethanol and 1-phenylethanol in 91 : 9 ratio[104].

The reaction of polymers of alkylthioboranes with diene hydrocarbons leads to the boron-containing heterocyclic compounds (see Section III. A. 4.).

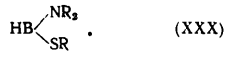
The trimers of alkylthioboranes do not react with unsaturated compounds at room temperature. When the reaction is carried out in boiling ether a complex mixture of substances is obtained. Thus in the reaction of the trimer of ethylthioborane (erroneously taken to be triethylthiodiborane) and oct-1-ene triethyl borate (10%), diethyl octylthioborate (20%), and ethyl dioctylthioborate (15%) are formed[116].

Dialkylthioboranes are less active hydroboronation agents than the polymers of alkylthioboranes. The reaction of dibutylthioborane with hex-1-ene, oct-1-ene, or cyclohexene takes place at room temperature and more rapidly on heating, and butyl esters of the corresponding alkylthioboric acids are obtained[73].

In the reaction of diphenylthioborane with styrene in tetrahydrofuran and the subsequent oxidation of the reaction products, 2-phenylethanol and 1-phenylethanol were isolated in 95 : 5 ratio with a yield of 77%.[104]

VI. DIALKYLAMINO(ALKYLTHIO)BORANES

An unusual class of mixed sulphur-containing compounds of boron is the dialkylamino(alkylthio)boranes (XXX):

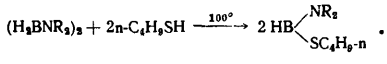


(XXX)

A. METHODS OF PREPARATION

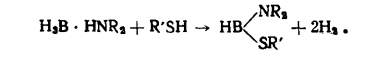
1. Synthesis of Dialkylamino(alkylthio)boranes from Dimers of Dialkylaminoboranes

Dialkylamino(alkylthio)boranes are obtained on heating dimers of dialkylaminoboranes with thiols[117,118]:

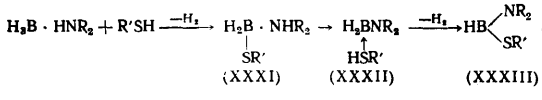


2. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylamine–Boranes

It is preparatively more convenient to obtain dialkyl amino(alkylthio)boranes by heating dialkylamine–boranes with thiols[117,119]. Reaction with liberation of hydrogen starts 70–80°C, proceeds vigorously at 100°C, and ends on briefly raising the temperature to 120–130°C

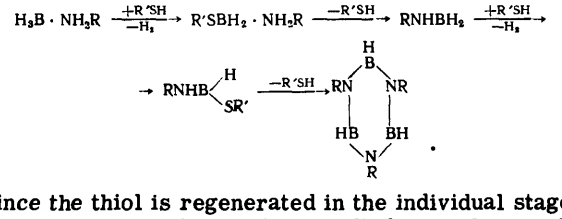


In the first stage of the reaction a complex of dialkylamine with alkylthio boranes (XXXI) is formed with liberation of hydrogen and is then converted into a complex of a dialkylaminoborane with a thiol (XXXII). The latter loses hydrogen to give the final product (XXXIII):



(XXXI) (XXXII) (XXXIII)

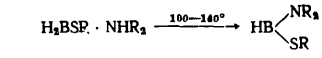
It should be noted that when heated with a thiol the complexes of borane with primary amines are converted into *N*-trialkylborazoles in high yield[120]



Since the thiol is regenerated in the individual stages of the reaction the synthesis of *N*-trialkylborazoles can be carried out using a catalytic amount of the thiol.

3. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylamine–Alkylthioboranes

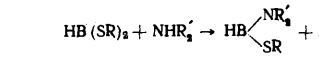
Complexes of the alkylthioboranes give, on heating with secondary amines, dialkylamino(alkylthio)boranes in 60–88% yield[110]:



The processes are complicated by side-reactions, as a result of which a thiol and a bis(dialkylamino)borane are formed.

4. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylthioboranes and Amines

Dialkylamino(alkylthio)boranes are obtained by the reaction of dialkylthioboranes and secondary amines[114]:



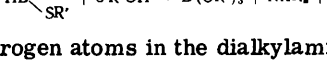
The reaction starts at room temperature and requires brief heating to complete it.

B. PROPERTIES

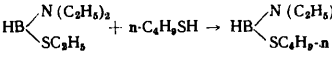
Dialkylamino(alkylthio)boranes are colourless mobile liquids with an extremely unpleasant odour, rather rapidly hydrolysed and oxidised in air. They are miscible with organic solvents in any proportions; they are not decomposed nor symmetrised at ~ 200°C. In the infrared spectra there are absorption bands in the range 2485–2500 cm^{-1}, corresponding to the B–H vibrations.

1. Reactions with Alcohols and Thiols

Dialkylamino(alkylthio)boranes react vigorously with alcohols at room temperature with liberation of hydrogen; initially the R_2N–and RS groups are replaced and then the dialkoxyboranes already formed are converted into borates[121]:

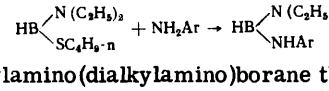


The hydrogen atoms in the dialkylamino(alkylthio)-boranes are not replaced by alkylthio-groups on heating with thiols, even up to 200°C. On using higher thiols re-esterification[12] occurs, like that which takes place in the esters of dialkylthioboric acids[52]:



2. Reactions with Amines

Dialkylamino(alkylthio)boranes with aromatic amines under mild conditions exchange an alkylthio-group for an arylamino-group[121]:



The arylamino(dialkylamino)borane thus formed reacts in its turn with an aromatic amine at 60–80°C, with the

arylamino-group replacing not hydrogen but the dialkylamino-group, as a result of which a bis(arylamino)borane is obtained:

$$HB\begin{matrix}N(C_2H_5)_2\\NHAr\end{matrix} + NH_2Ar \rightarrow HB(NHAr)_2 + NH(C_2H_5)_2 .$$

Similarly, under the action of primary aliphatic amines, bis(arylamino)boranes are obtained[118]:

$$HB\begin{matrix}N(CH_3)_2\\SR'\end{matrix} + 2NH_2R \rightarrow HB(NHR)_2 + NH(CH_3)_2 + R'SH .$$

The reaction of dialkylamino(alkylthio)boranes with secondary amines is peculiar[121,122]. When diethylamino-(butylthio)borane is heated with diethylamine the equilibrium:

$$HB\begin{matrix}N(C_2H_5)_2\\SC_4H_9\text{-}n\end{matrix} + NH(C_2H_5)_2 \rightleftarrows HB[N(C_2H_5)_2]_2 + n\text{-}C_4H_9SH$$

is established.

Heating bis(dimethylamino)borane with butylthiol leads to the same equilibrium mixture. In this last instance a dialkylamino-group at the boron atom is replaced by an alkylthio-group, whereas the reverse process—the replacement of the RS group by the R_2N group—usually occurs, as in the action of amines on esters of organothioboric acids[63,87]. The above equilibrium can be displaced completely to the right if the amine used boils at a higher temperature than the thiol product, which can then be distilled from the reaction mixture:

$$HB\begin{matrix}N(C_5H_{11}\text{-iso})_2\\SC_3H_7\text{-}n\end{matrix} + NH(C_5H_{11}\text{-iso})_2 \rightarrow HBN(C_5H_{11}\text{-iso})_2 + n\text{-}C_3H_7SH .$$

Under the action of an equimolecular amount of methylaniline on diethylamino(butylthio)borane both the RS–and R_2N–groups are replaced, and half the original organoboron compound remains. At a reagent ratio of 1 : 2, bis-(*N*-methyl-*N*-phenylamino)borane is obtained in 83% yield[122].

The low mobility of the hydrogen atom in dialkylamino-(alkylthio)boranes also appears in their inability to add to alkenes even under comparatively severe conditions in which the dimer of diethylaminoborane hydroborates but-1-ene and oct-1-ene[117]. Hence the ease of nucleophilic replacement of various groups at the boron atom in dialkylamino(alkylthio)boranes decreases in the following series: RS > NR_2 > H.

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As the above shows, sulphur-containing organic compounds of boron exhibit increased reactivity in comparison with their oxygen analogues, expressed in their tendency to form complexes and exchange RS groups for other groupings. This is explained, on the one hand, by the lower ionisation potential[123] of the unshared pair at the sulphur atom (13.64 eV) in comparison with oxygen (18.70 eV), and on the other by the relatively low value of the energy of the B–S bond ($\sim$ 70 kcal mole^{-1})[5] compared with that of the B–O bond (110–115 kcal mole^{-1}) and at the same time there is the similarity in the energies of the N–H (85 kcal mole^{-1}), B–N (80 kcal mole^{-1}), and S–H (87 kcal mole^{-1}) bonds[124]. Because of this, reactions with breaking of B–S bonds, leading to the formation of bonds between the boron and other elements (N, O), seem energetically favourable.

Readily accessible alkylthioborates which are smoothly obtained from boron trichloride and thiols in the presence of tertiary amines seemed suitable for the synthesis of various classes of sulphur-containing esters of organothioboric acids. In turn these esters can be used with success in the synthesis of various other types of organoboron compounds.

A feature of the methods of synthesis developed is that Grignard reagents are not used. The starting compounds are boron trialkyls, obtainable from diborane and alkenes, which by a combination of new synthetic procedures are readily converted into reactive sulphur-containing organoboron compounds, which can then be used for further syntheses. A second source of organoboron compounds is the "alkylthioboranes" obtainable from diborane and thiols, which are of independent theoretical interest in the chemistry of boron.

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Electron Transfer as an Elementary Act of Organic Reactions

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Many heterolytic reactions are often accompanied by radical processes and contrariwise the reactions of radicals in many instances lead to the formation of ions. The simultaneous occurrence of homolytic and heterolytic processes cannot be explained from the viewpoint of the now generally accepted theory of organic reactions. These contradictions can be easily resolved if it is assumed that the formation of a new bond is preceded by the transfer of an electron from one reacting entity to another.

In the present work on the basis of voluminous literature material the conclusion is drawn that electron transfer processes actually play an important part in many organic reactions (reactions with free metals, some substitutions, etc.).

The influence of various factors on electron transfer processes is examined. Assumptions concerning the relative role of these processes in the formation and reactions of organometallic compounds are advanced. There is a bilbiography of 242 references.

CONTENTS

I. Introduction	954
II. Formation of stable radical-ions	955
1. Reduction by metals	955
2. Electrochemical reactions	955
3. Anions as donors of an electron	956
4. Neutral molecules as donors of an electron	957
5. Radicals as donors of an electron	958
III. Reactions of radical-ions	959
1. Radical-ions as donors and acceptors of an electron	959
2. Reaction of radical-ions accompanied by a change in the structure of the initial molecule	959
IV. Reactions which proceed through the intermediate formation of radical-ions	960
1. Cleavage of carbon–element bonds	960
2. Substitutions	962
3. Other reactions	964

I. INTRODUCTION

Many of the concepts of contemporary theoretical chemistry built up in the first half of the XXth century and which are indisputably of use in chemistry need not now be regarded as absolute. This relates, for example, to attempts to positively divide reactions which really proceed according to a cyclic transfer scheme into electrophilic and nucleophilic[1,2]. Frequently on the basis of such a division one of the reacting species is essentially regarded arbitrarily as the "reagent" and the other as the "substrate". Dessy and Paulik[2] recently criticised the expediency of such a categoric classification for examples of a multicentre mechanism.

The same uncertainty arises also in attempts to divide strictly reactions into homolytic and heterolytic. Usually the problem of the homolytic or heterolytic nature of a process becomes unnecessary ultimately. In most instances only the fact of the formation of radical products in ionic reactions (or, contrariwise, the production of ions in free radical reactions) is stated but these processes are regarded as side-reactions which proceed in parallel with the main reaction.

Apparently such a contradiction can be resolved if it is assumed that the formation of a new bond is preceded by the transfer of electrons from one reacting species to another (by virtue of a difference in electron affinity and the greater mobility of the electron cloud in comparison with the nuclei or entire fragments of the molecules). Assumptions of this type are sometimes regarded as one of the possible approaches to the classification of organic reactions[3], but really these considerations have until recently not been taken into account in examining particular mechanisms.

In examining different electrochemical processes, Semenov[4] noted that "... strictly speaking, in a single act one electron is transferred, since the simultaneous transfer of two electrons is a much less probable event". Despite the considerable differences between chemical changes and electrode processes, this position, it seems to us, must be taken into account in studying organic reactions when the sources of electrons are metals, ions, or neutral molecules.

Heterolytic breaking of a non-ionic bonds with not too pronounced solvation effects is energetically less favourable than homolytic breaking, since in the first instance additional energy is needed for the preliminary polarisation of the bond[5,6]. More and more information is becoming available showing that the so-called homolytic dissociation is usually a minimum bimolecular process[7,8] and one of the reagents can also serve to localise an electron[9].

Electron transfer is a widely distributed phenomenon in inorganic redox reactions and various photochemical and radiation-chemical processes[10,11].

Finally, extensive although insufficiently systematised material about organic reactions of electron transfer is being accumulated and the tempo of the increase in new facts in this region is so high that the idea naturally arises that reactions of this type actually permeate the whole of organic chemistry including the field of "classical" heterolytic reactions.

This article is an attempt to generalise and systematise these facts, although it is hardly possible to deal with them exhaustively within the framework of the present review.

II. FORMATION OF STABLE RADICAL-IONS

The most typical electron transfer reactions, where the very fact of the transfer of just one electron is unquestioned, are reactions for the formation of radical-ions (RI). Since in this instance the electron transfer is usually not complicated by side-processes and the RI itself is readily identified by EPR methods and ultraviolet spectroscopy, these reactions are an extremely convenient model for studying electron transfer in organic reactions. Some typical examples of monoelectron transfer reactions are given in Table 1.

Table 1. Types of electron transfer.

Reaction	Electron donors	Electron acceptors (EA)
Reduction by metals	M = alkali or alkaline earth metals or its amalgam	aromatic and heterocyclic compounds, arylalkyl and diaryl ketones, imines of diaryl ketones, nitro-compounds, some organoelemental compounds
Electrochemical reduction	cathode	ditto
Electrochemical oxidation	aromatic hydrocarbons, amines	anode
Reduction by anions	organometallic compounds of active metals, alkoxides, iodide ion	aromatic compounds, diaryl ketones, aromatic diazo-compounds, tetracyanoethylene, nitro-compounds
Reduction by Lewis bases	aromatic hydrocarbons, amines, alkenes	nitro-compounds, tetracyanoethylene, stable radicals, carbonium ions
Oxidation	aromatic hydrocarbons, amines, metallocenes, free radicals	conc. H_2SO_4, $AlCl_3 + CH_3NO_2$, $SbCl_5$, tetracyanoethylene, heavy metal cations, nitro-compounds

A large number of organic compounds of different classes exhibit the capability to receive one electron with the formation of anionic radicals (AR).[12] This relates to aromatic[13-16] and heterocyclic[11-20] systems and also to systems which contain conjugated bonds[21-23] and electron-withdrawing groups[24,25]. Initial reports of the production of AR of cyclopropane, adamantane, hexamethylenetetramine, spiropentane, and 1-methyladamantane proved erroneous[26].

Reports recently appeared about the production of a series of organoelemental AR, containing boron[27,28], silicon[29,30], germanium[30], nitrogen[31,32], phosphorus[33-35], and transition metals[36].

Under the action of oxidants, aromatic[37] and heterocyclic[38] compounds and also some amines[39-40] can give up one electron to form cationic radicals (CR).

1. Reduction by Metals

Historically the first and therefore now the most developed method of production of stable AR are reactions with free metals. The ease of formation of AR depends on a series of factors, the most important of which are the affinity of the acceptor for an electron, the solvating capability of the medium, and the donor ability of the electron source. In a series of aromatic hydrocarbons the capability for reduction rises on going from benzene to condensed aromatic hydrocarbons: benzene < biphenyl < < naphthalene < anthracene < tetracene[41,42]. The introduction of electron-withdrawing substituents also acts in the same direction. The ease of transfer of an electron to the molecule of the acceptor from a metal is determined by the donor capability of the latter. However, the quantitative evaluation of this capability encounters considerable difficulties: in particular it is impossible to use standard electrode potentials in water, the photochemical work function, etc. In most instances alkali or alkaline earth metals or their amalgams[12] are used for reduction, but when the acceptor molecule has a sufficiently high electron affinity heavy metals can also act as reductant. For example, tetracyanoethylene forms an AR on reduction with copper powder[43]:

$$(CN)_2C{=}C(CN)_2 + Cu \rightarrow [(CN)_2C{=}C(CN)_2^{\cdot-}Cu^+ .$$

In the alkali metal series lithium seems the best reductant for most instances. In dimethoxyethane the reaction of biphenyl with sodium is equilibrium ($K \simeq 10^{-2}$),[44] whereas a dianion is formed with lithium under these conditions[45]:

$$C_{12}H_{10} + Na \underset{}{\overset{DME}{\rightleftharpoons}} C_{12}H_{10}^{\cdot-} + Na^+$$

$$C_{12}H_{10} + Li \xrightarrow{DME} C_{12}H_{10}^{2-} + 2Li^+ .$$

This can be explained by the greater solvation of the lithium cation compared with the cations of its analogues in the Group[46], which appears, in particular, in the fact that lithium, unlike sodium, is soluble in tetrahydrofuran[47]. In the general case the ease of formation of similar AR in various ethers changes symbathically with the solubility in these ethers of alkali metals or of K/Na alloy[47-53]. Probably, in the formation of the AR the solvent plays the part of a carrier of an electron from the metal to the molecule of the acceptor†. Hexamethyltriamidophosphate exhibits the greatest dissolving ability in relation to alkali metals (up to 1 M),[53,54] however, unfortunately the influence of this solvent on the formation of AR has not yet been studied. The important and sometimes also the decisive part of the medium in the formation of AR can be illustrated by a series of examples. Thus whereas in DME naphthalene is reduced by sodium to an AR,[57] in liquid ammonia a dianion is formed[58]. Similarly magnesium does not reduce naphthalene in ethers, whereas in liquid ammonia naphthalenemagnesium is formed[59]; trimesitylboronsodium, which exists in benzene solution as a diamagnetic dimer, dissociates on the addition of tetrahydrofuran[27].

2. Electrochemical Reactions

A review was recently published about the mechanism of electrochemical reactions[60], therefore we will consider here only certain examples dealing with the formation of RI in electrode processes. AR of naphthalene[61], anthracene, biphenyl, chrysene, fluoranthene[62], azulene[63], substituted benzenes[63], benzophenone[64], and fluorenone[65] were obtained by electrochemical reduction.

In many instances electrochemical methods have definite advantages over other methods of generating AR.[40,66]

† It is known, however, that potassium also reacts with aromatic compounds in a hydrocarbon medium[55,56].

Carrying out the electrolysis in the microwave cavity of an EPR spectrometer allowed extremely unstable IR to be identified, the experimental detection of which by other methods would be extremely complicated. This relates, for example, to the production of the AR of butadiene[21] and certain organoelemental compounds[36], and the CR of *p*-phenylenediamine[66] and triethylenediamine[40]. The use of electrochemical methods allowed the effect of various solvents (including protic solvents) on the distribution of unpaired electron density in various AR to be investigated[68,69]. In several instances EPR spectra with a high degree of resolution were obtained[70].

Interesting results have been obtained in investigating the polarographic reduction of halogenonitrobenzenes[71]. It was found that with iodonitrobenzenes only the spectrum of the AR of nitrobenzene is observed, whereas the formation of an AR precedes the loss of an iodide ion. With the bromonitrobenzenes a bromide anion is detached only from the *ortho*-position; chloronitrobenzenes form stable AR. In drawing attention to the undoubted similarity between electrochemical reduction and reactions with free metals it can be suggested that the first act in the reduction of halogen derivatives by metals is also the transfer of an electron and the formation of AR (see p. 962).

3. Anions as Donors of an Electron

A large number of examples are known when the donors of an unpaired electron are diamagnetic anions: carbanions[72-77], dihydro-derivatives of aromatic compounds in the presence of bases[78,79], alkoxide ions[80,81], the hydroxide ion[82,83], and the iodide ion[84].

An acceptor of an unpaired electron can be neutral molecules (A)

$$B^- + A \rightarrow B^{\cdot} + A^{\cdot -}$$
$$B^{2-} + A \rightarrow B^{\cdot -} + A^{\cdot -};$$

free radicals formed with sufficient electron affinity:

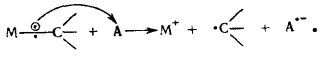
$$B^- + R^{\cdot} \rightarrow B^{\cdot} + R^-$$
$$B^{2-} + R^{\cdot} \rightarrow B^{\cdot -} + R^-;$$

ions:

$$B^- + R^+ \rightarrow B^{\cdot} + R^{\cdot}$$
$$B^- + B^{1-} \rightarrow B^{\cdot} + B$$

etc.

The potential carbanion of active organometallic compounds can also play the part of anions B^-, that is, in other words, a polar metal–carbon bond:

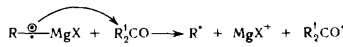


Apparently the first established instance of the transfer of a single electron from an anion to a neutral organic molecule is a reaction studied by Schlenk and coworkers[85,86], that between triphenylmethylsodium and diaryl ketones, leading (after hydrolysis and oxidation by atmospheric oxygen) to triphenylmethyl peroxide and pinacones:

$$(C_6H_5)_3C^- + Ar_2CO \rightarrow (C_6H_5)_3C^{\cdot} + Ar_2\dot{C}-\bar{O}.$$

Triphenylmethylmagnesium bromide reacts similarly[87].

The suggestion made by Arbuzov and Arbuzova about the free radical nature of the reaction of cyclohexylmagnesium bromide with benzophenone[88] is essentially equivalent to an assumption concerning the possibility of single-electron transfer in the reaction of Grignard reagents with ketones:



Indirect arguments in support of the stepwise nature of such reactions were found in subsequent years. The intermediate formation of ketyl was recently proved by the EPR method by the example of the reaction of a series of substituted benzophenones with ethylmagnesium iodide and phenylmagnesium bromide[76].

A single-electron transfer was observed in the reaction of triphenyltinlithium with benzophenone, carbon dioxide, and sulphur dioxide[74]. Streitwieser and Lawler noted the formation of AR of anthracene in investigating deuterio-exchange, which can be catalysed by lithium cyclohexylamide[89].

Organolithium compounds reduce certain aromatic hydrocarbons (for example, anthracene[77]) with the formation of the corresponding AR:

$$RLi + ArH \rightarrow R^{\cdot} + Li^+ + ArH^{\cdot -}.$$

The ability of organolithium compounds to transfer a single electron changes symbatically with their ease of oxidation[90], evidently by virtue of the similarity in the mechanisms of these reactions. For example, in going from primary to secondary, and further to tertiary radicals R, the rate of oxidation and the ease of electron transfer increase. According to Russell, this is connected with the decrease in the stability of the carbanion and the increase in the stability of the corresponding radical in this series. It is characteristic that the AR of tolane could be observed in the action of t-butyl-lithium on tolane but not of n- or s-butyl-lithium[91].

Table 2. Decomposition potentials of Grignard reagents in 1 M ethereal solution.

R in RMgX	Decomposition potential, V	R in RMgX	Decomposition potential, V
C_6H_5	2.17	$C_6H_5(CH_3)CH$	1.24
CH_3	1.84	$(CH_3)_2CH$	1.07
C_3H_7	1.42	$(CH_3)_3C$	0.97
C_4H_9	1.32	$CH_2=CHCH_2$	0.86
C_2H_5	1.28		

A searching quantitative appraisal of the donor ability of organometallic compounds can evidently be obtained by using their electrochemical oxidation potential, but information on this question is scanty[92-94]. Evans[92,93] determined the decomposition potentials of ethereal solutions of alkylmagnesium halides (Table 2). If it is assumed that in a series of corresponding organo lithium compounds an analogous picture will be obtained, then it can be expected that depending on the type of radical the donating ability of the alkyl-lithiums will increase in the order: CH_3 < higher alkyls < allyl < benzyl. Actually, the rate of formation of the AR increases in the order CH_3Li, $C_6H_5Li \ll C_4H_9Li < C_6H_5CH_2Li$.[73]

The transfer of an unpaired electron from an organometallic compound is greatly increased under ultraviolet irradiation, Thus on irradiating the C_6H_5Li–ArH system the rate of formation of the AR $ArH^{\cdot -}$ is increased by a factor of 10^5.[75]

An important condition for the single-electron transfer from an anion to a neutral molecule is a sufficiently great difference between the values of the electron affinity of the donor and the acceptor. As noted above, organolithium

compounds reduce aromatic hydrocarbons[77], and organomagnesium compounds reduce diaryl ketones[76,95]. Although apparently weaker reductants than organometallic compounds of the active metals, nevertheless alkoxide ions are capable of reducing aromatic ketones and nitro-compounds[80,95].

The reduction of diaryl ketones and nitro-compounds by alkoxides is also accelerated by irradiation, and the concentration of the AR formed is determined by the intensity of the irradiation[96]:

$$ArNO_2 + RO^- \xrightarrow{h\nu} ArNO_2^{\cdot -} + RO^{\cdot}$$

$$Ar_2CO + RO^- \xrightarrow{h\nu} Ar_2CO^{\cdot -} + RO^{\cdot}.$$

Tetracyanoethylene[43] and tetracyanoquinodimethane[98], which exhibit a very high electron affinity, are readily oxidised by even the iodide ion:

$$I^- + (CN)_2C{=}C(CN)_2 \rightarrow {}^1/_2 I_2 + [(CN)_2C{=}C(CN)_2]^{\cdot -}$$

$$I^- + (CN)_2C{=}\langle\rangle{=}C(CN)_2 \rightarrow {}^1/_2 I_2 + \left[(CN)_2C{=}\langle\rangle{=}C(CN)_2\right]^{\cdot -}.$$

The hydroxide ion reacts similarly, also reducing *p*-quinone, chloroanil, and duroquinone[82,83,97,99].

Many acetylenic compounds are also rather strong acceptors in relation to the anions I^-, CN^-, and SCN^- in dimethylformamide medium[100]:

$$A^- + RC{\equiv}CR' \rightarrow [RC{\equiv}CR']^{\cdot -} + A^{\cdot}$$

where A = I, CN, or SCN.

It was noted above that in the dissolution of aromatic nitro-compounds in alcohol–dimethylsulphoxide mixture in the presence of alkali metal alkoxide the EPR signal of the corresponding AR is observed, but the degree of electron transfer‡ is relatively low (~ 0.1%). Since under these conditions many conjugated acids are converted into anions this allowed us to evaluate the relative donating ability of a series of anions[95] (Table 3). The data in Table 3, however, allow only an approximate estimation of the relative donor ability of the various sources of an unpaired electron, since these values are greatly dependent upon the degree of ionisation of the initial compound under the action of an alkoxide:

$$BH + RO^- \rightarrow B^- + ROH,$$

and also of the side-reactions, the importance of which depends upon the nature of the donor. The nature of the acceptor is also far from being unimportant. Thus in relation to nitrobenzene, cyclopentadienes are arranged in the order: cyclopentadiene < fluorene < indene, whereas in relation to azobenzene the order is different: cyclopentadiene < indene < fluorene[95]. Whereas organolithium compounds are frequently better reductants than the corresponding organomagnesium compounds the observable degree of electron transfer in benzofurazane and benzo[*c*]indolene is significantly greater for alkylmagnesium halides.

The restrictions associated with side-processes which accompany the transfer of an electron from an anion to an acceptor molecule are reduced to a minimum in studying electron transfer reactions between dianions and the corresponding hydrocarbons[42,101,102]:

$$B^{2-} + B \rightarrow 2B^{\cdot -}.$$

In many instances instead of dianions it is possible to use the corresponding dihydro-derivatives in the presence of strong bases[78,103–108]. Exceptions are the 1,4-dihydronaphthalene–naphthalene and 1,4-cyclohexadiene–benzene systems in which the AR were not observed. This departure is evidently explained by the fact that under these reaction conditions ionisation of the 1,4-dihydronaphthalene and 1,4-cyclopentadiene does not take place.

‡ The degree of electron transfer = [AR] × 100/[acceptor] %.

Table 3. Degree of electron transfer* from anions to aromatic nitro-compounds.

Donors[a]	Acceptor[b], degree of electron transfer, % (5 min)	
	nitrobenzene[c]	m-dinitrobenzene[d]
Pure solvent	0.1 (10 min)	0.1 (20 min)
Fluorene	13	40.80 (2 min)
Indene	36	—
Cyclopentadiene	0.8	2.6
Acetophenone	0.8	2.7
Propiophenone	91	4
Benzoin	100[f]	—
Bluoren-9-ol	100[f]	—
1,4-Hydroquinone	40[f]	100[f]
Thiophenol	0.2 (30 min)	0.6
3,4-Dimercaptotoluene	11	58
Nitroethane	0.6	2
N-Hydroxybenzenesulphamide	92	10[e] (10 min)
Hydrazobenzene	2 (40 min)	7.5[e] (2 min)
Benzophenone ketyl[h]	100	6.8 (3 min)
n-Butyl-lithium[i]	6	

* See note

a) Concentration of donor 0.025 M, concentration of base 0.05 M;
b) Concentration of acceptor 0.005 M.
c) Dimethyl sulphoxide (20%)–t-butyl alcohol (80%).
d) In ethanol (EPR spectrum does not correspond with the AR of the acceptor
e) [Not given in Russian (Ed. of Translation)].
f) EPR spectrum of the AR of the donor predominates.
g) Spectra of both AR are observed.
h) Obtained in the dissociation of saturated solution of benzpinacone.
i) 1 M solution in a mixture of tetrahydrofuran (75%) and hexane (25%).

Stable radicals are effective electron acceptors but reactions of this type have hardly been studied at all. From the broadening of the hyperfine structure lines of the EPR spectrum Weissmans and coworkers[109] found the presence of electron exchange between the tris-(*p*-nitrophenyl)methyl radical and the corresponding anion:

$$(p\text{-}NO_2C_6H_4)_3C^{\cdot} + (p\text{-}NO_2C_6H_4)_3C^- \rightleftarrows (p\text{-}NO_2C_6H_4)_3C^- + (p\text{-}NO_2C_6H_4)_3C^{\cdot}.$$

Depending on the solvent the rate constant varies within the limits 10^7–10^9 litre mole^{-1} s^{-1} and the activation energy from 0.9 to 2.3 kcal mole^{-1}.

4. Neutral Molecules as Donors of an Electron

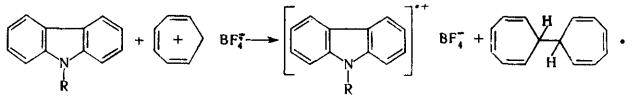
A large number of aromatic and heterocyclic compounds, and also compounds which contain a hetero-atom, have an unshared pair of electrons (many, a nitrogen atom) capable of acting as a donor of an electron in relation to a strong oxidant, forming a CR.

For example, triphenylamine is readily oxidised by iodine in the presence of silver perchlorate with the formation of a coloured paramagnetic solution of triphenyliminium perchlorate $(C_6H_5)_3NH^{\cdot +}ClO_4^-$.[110] Other aromatic amines behave similarly[111,112]. CR of *p*-phenylenediamine[66,67] and its alkyl-substituted derivatives[39,113], triethylenediamine[40], tetrakis(dimethylamino)ethylene[114], and several other amines were obtained by electrochemical oxidation.

Electron transfer was observed for the reaction between aliphatic amines and trinitrobenzene[113,115], tetracyanoethylene, and tetracyanoquinodimethane[116]. Many complexes of aromatic amines are paramagnetic even in the solid state. The complexes of tetramethyl-*p*-phenylenediamine with benzoquinones and tetracyanoquinodimethane dissociate in solvating solvents, forming the corresponding CR and AR.[78,117,118] The complexes of tetracyanoethylene[43,66] behave similarly. Tetramethyltetrazene is oxidised by tetranitromethane into the corresponding CR:[119]

$$(CH_3)_2NN{=}NN(CH_3)_2 + C(NO_2)_4 \rightarrow [(CH_3)_2NN{=}NN(CH_3)_2]^{\cdot+} + [C(NO_2)_4]^{\cdot-}.$$

Carbonium ions can act as the electron acceptor. Thus tropylium tetrafluoroborate oxidises carbazole and *N*-methylcarbazole to the corresponding CR:[120]

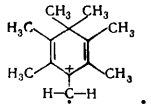


The CR themselves can act as oxidants in relation to other amines having less electron affinity than amines corresponding to the given CR. Thus the CR of *NN'*-tetramethylbenzidine is reduced by *p*-phenylenediamine and its *NN'*-tetramethyl derivative[121]:

$$[(CH_3)_2NC_6H_4C_6H_4N(CH_3)_2]^{\cdot+} + (CH_3)_2NC_6H_4N(CH_3)_2 \rightarrow (CH_3)_2NC_6H_4C_6H_4N(CH_3)_2 + [(CH_3)_2NC_6H_4N(CH_3)_2]^{\cdot+}.$$

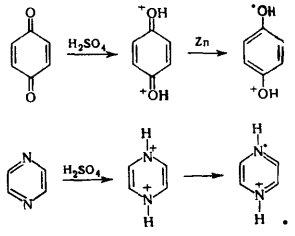
The oxidation of aromatic and heterocyclic compounds can be brought about both electrochemically and by chemical means[122-125].

The oxidants used are: 98% sulphuric acid[126,127], alkyl- or aryl-sulphonic acids[128], antimony(V) chloride[129,130], and aluminium chloride in nitromethane solution[131]. Sulphuric acid is a relatively weak oxidant, therefore the CR concentration is usually low. Thus with anthracene only 1% of the total amount of hydrocarbon introduced is oxidised. With $SbCl_5$ the oxidation is almost complete. In the action of $SbCl_5$ on an excess of anthracene in methylene chloride an adduct of CR with the neutral molecule is formed $(C_{10}H_{12})_2^{\cdot+}SbCl_4^-$.[130] When sulphuric acid acts on hexamethylbenzene a CR related to the heptamethylbenzonium cation is formed[132]:



The same CR is formed in the reaction of iodine and antimony(V) chloride.

The CR of the semiquinone type are formed in the reduction of dicarbonyl compounds and of related nitrogen heterocycles in an acid medium[133]. For example, for *p*-benzoquinone and piperazine:



Analogous CR are obtained from 1,4-naphthoquinone, anthraquinone, phenazine, 4,4'-bipyridyl, and certain α-diketones[134-136].

Strong π-acids of the tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCQ) type react with aromatic hydrocarbons to form the corresponding AR and CR:[43,98]

$$ArH + TCNE \rightarrow ArH^{\cdot+} + TCNE^{\cdot-}$$

With tetracyanoquinodimethane, complexes of the composition $ArH^+(TCNQ)^-$ (TCNQ) are also formed[98].

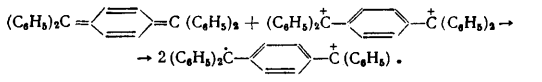
The biscyclopentadienyls of cobalt and iron are oxidised by TCNE and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to the corresponding metallocinium cations[107,137]:

$$(C_5H_5)_2M + TCNE \rightarrow (C_5H_5)_2M^+ + TCNE^{\cdot-}$$

where M = Fe, Co. The position of the equilibrium depends greatly on the solvent[137].

The formation of paramagnetic products, probably the result of electron transfer, was noted in the reaction of tetranitromethane with 2,3-dimethylbutadiene, cyclohexadiene, and isoprene[138].

One of the reliably established examples of the donor capability of a conjugated system of double bonds is the single-electron transfer from tetraphenylquinodimethane to a dicarbonium ion from tetraphenyl-*p*-xylene[139]:

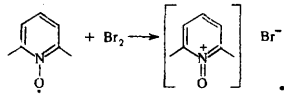


5. Radicals as Donors of an Electron

Free radicals, which exhibit high electron affinity usually emerge as vigorous oxidants. However, the available experimental data suggest that free radicals in the accepted sense are amphoteric, that is, capable both of capture of an electron not supplied to the carbanion and of the supply of an unpaired electron to a sufficiently strong acceptor with the formation of a corresponding cation. The best known example of the donor ability of free radicals is the reduction of heavy metal salts by the triphenylmethyl radical[140]:

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

Stable *N*-oxide radicals are readily oxidised by bromine to form immonium cations[141]:



Bulê and Norman[142], in investigating the reaction of formaldehyde and acetaldehyde with hydroxyl radicals, found that with an excess of the aldehyde the EPR spectrum of the AR of the corresponding aldehyde is observed. On adding nitrobenzene to the reaction mixture the EPR spectrum of a nitrobenzene AR was observed. These results formed a basis for the hypothesis that a hydrated form of a primary radical, produced in the removal of a hydrogen atom from a molecule of the aldehyde, is capable of reducing a neutral molecule of the aldehyde or nitrobenzene:

$$RCH(OH)_2 + \cdot OH \rightarrow RC(OH)_2,$$
$$R\dot{C}(OH)_2 + RCHO \rightarrow RCO_2H_2^+ + R\dot{C}HO \rightleftarrows RCOOH + R\dot{C}HOH,$$

or

$$R\dot{C}(OH)_2 + C_6H_5NO_2 \rightarrow RCO_2H_2^+ + C_6H_5NO_2^{\cdot-}.$$

III. REACTIONS OF RADICAL-IONS

The reactions of RI, the high chemical activity of which is due to the presence of an unpaired electron, can be divided into two groups. The first type comprises the reactions in which RI participate only as donors (or acceptors) of an electron (reactions with organic halides, the initiation of polymerisation, exchange reactions, etc.). During the course of these reactions the skeleton of the RI molecule does not undergo any changes. The second class of reaction includes a large number of conversions of RI which lead to a fundamental reconstruction of the initial molecule (hydrolysis, alkylation, decomposition of the RI, etc.).

1. Radical-ions as Donors and Acceptors of an Electron

Typical representatives of this type of reaction are the exchange reactions of RI with neutral molecules[121,143-145]:

$$ArH + ArH^{\cdot-} \rightleftarrows ArH^{\cdot-} + ArH,$$
$$ArH^{\cdot+} + ArH \rightleftarrows ArH + ArH^{\cdot+}.$$

Weissmann and coworkers[143] first showed that exchange by an electron appears in a broadening of the hyperfine structure lines of the EPR signal, the increase in breadth depending significantly on the concentration of the neutral compound. The changes in the EPR spectra were used to calculate the rate constants of the exchange[144,145]. Exchange reactions between stable AR and various acceptors[40,41,122] of the type:

$$ArH^{\cdot-} + Ar'H \rightleftarrows ArH + Ar'H^{\cdot-}$$

were also studied and it was shown that the position of the equilibrium depends on the difference in potentials of the polarographic reduction of the two partners[121].

Reactions of AR with organic halides have been studied in the greatest detail. In these reactions the AR act as an effective donor of an electron. The primary act of the reaction is the transfer of an electron from the AR to the halide molecule with the formation (probably through the intermediate formation of an AR of the halogen derivative) of a hydrocarbon radical and a halide ion[146-149]:

$$ArH^{\cdot-}M^+ + RX \rightarrow ArH + [RX^{\cdot-}M^+] \rightarrow R^{\cdot} + X^- + M^+.$$

The subsequent fate of radical R is determined by its structure and the conditions under which the process is carried out. In carrying out the reaction of the AR of naphthalene with an equimolecular mixture of two alkyl halides, RX and R'X, a mixture of the hydrocarbons RR, RR', and R'R' is formed in the ratio 1 : 2 : 1, together with appreciable quantities of RH and R_{-H}.[147] The ratio of the products of dimerisation (R–R) and of the products of the reaction of the radical with the solvent depends greatly on the nature of the halogen atom. Thus in the system $n\text{-}C_5H_4X + C_{10}H_8^{\cdot-}Na^+$, on going from n-pentyl chloride to the iodide the quantity of n-pentane decreases from 43.9 to 17.3% and the yield of n-decane increases from zero to 55.7%. The reaction of hexenyl halides with naphthalenesodium is accompanied by a rearrangement of the hexenyl radical formed into the cyclopentylmethyl radical[149]. With certain aromatic and aliphatic-aromatic halides the reaction with the AR leads to products of a Wurtz reaction with rather high yields (bibenzyl 30, bibenzhydryl 71, bi-2-naphthyl 71, biphenyl 90%)[148]; the initial aromatic hydrocarbon can be used in catalytic amounts.

Spectrophotometric investigation of the reactions of AR with various alkyl halides showed that the reaction is second order overall, first with respect to each of the reagents[150-152].

Since during the course of the reaction the organically bound halogen is converted into a halide ion, this method could be used for the quantitative determination of halogen in organic compounds[153,154].

Alkyl tosylates are split by the naphthalene AR with formation of the corresponding alkoxides and salts of toluene sulphinic acid. The yield of alcohols (after hydrolysis) is almost quantitative. Under the action of an excess of AR the sulphinic acid is reduced to toluene[155]:

$$p\text{-}CH_3C_6H_4SO_3OR + C_{10}H_8^{\cdot-}Na^+ \rightarrow p\text{-}CH_3C_6H_4SO_2^-Na^+ + RONa \xrightarrow{\text{excess } C_{10}H_8^{\cdot-}Na^+} CH_3C_6H_5.$$

Under the action of inorganic oxidants the AR also very readily give a surplus electron. In oxidation by atmospheric oxygen the original hydrocarbon and the alkali metal peroxide are formed, for example[156]

$$2C_{10}H_8^{\cdot-}Na^+ + O_2 \rightarrow 2C_{10}H_8 + Na_2O_2.$$

Under these conditions cobalt(II) chloride is reduced with the formation of colloidal cobalt, which ignites in air[157]. The reducing action of AR finds application for obtaining highly reactive manganese, used for making manganese carbonyl[158].

2. Reaction of Radical-ions Accompanied by a Change in the Structure of the Initial Molecule

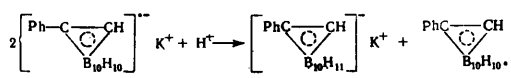
The overwhelming majority of AR are stable only in aprotic media. The addition of protic solvents causes a rapid disappearance of a characteristic signal in the EPR spectrum. With the AR of aromatic hydrocarbons the main products are the corresponding dihydro-derivative and the initial hydrocarbon (mixture ~ 1 : 1):[156,159]

$$ArH^{\cdot-} + H^+ \rightarrow ArH_2^{\cdot},$$
$$ArH_2^{\cdot} + ArH^{\cdot-} \rightarrow ArH_2^- + ArH,$$
$$ArH_2^- + H^+ \rightarrow ArH_3.$$

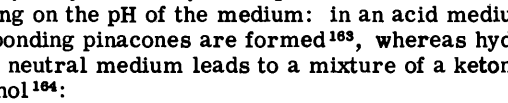
In the addition of a proton to the AR of an aromatic hydrocarbon the $ArH_2^{\cdot}$ radical is formed, which exhibits a greater electron affinity than the molecule of the initial hydrocarbon[160], which is subsequently reduced further by the excess of AR to the corresponding anion. If the anion formed is sufficiently stable (as it is, for example, in the alcoholysis of triphenylboronsodium) the reaction stops at this stage[161]:

$$2Ph_3B^{\cdot-}Na^+ + CH_3OH \rightarrow [Ph_3BH]\,Na + [Ph_3BOCH_3]\,Na.$$

The hydrolysis of the AR of phenylbarene proceeds analogously[162]:



The hydrolysis of ketyls can proceed in two directions, depending on the pH of the medium: in an acid medium the corresponding pinacones are formed[163], whereas hydrolysis in a neutral medium leads to a mixture of a ketone and an alcohol[164]:



The hydrolysis of dianions of aromatic hydrocarbons which are formed during the subsequent reduction of the

AR leads to the same products as the hydrolysis of the AR:[165,166]

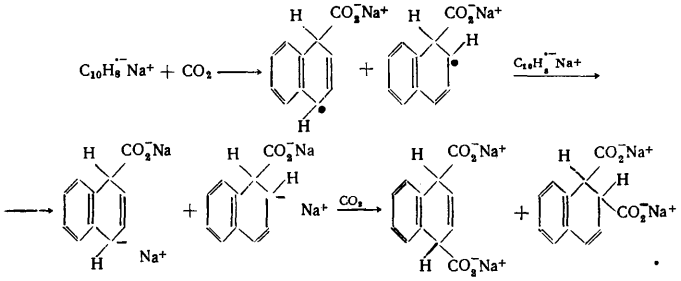
$$ArH^{2-} + H^+ \rightarrow ArH_2^-,$$
$$ArH_2^- + H^+ \rightarrow ArH_3.$$

The mono-anions which are formed in the addition of a proton to a dianion are identical with anions formed in the hydrolysis of the AR. Depending on the nature of the initial hydrocarbon these monoanions disproportionate in solution by one of the following schemes:

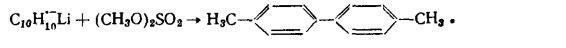
$$2ArH_2^- \rightarrow ArH_3 + ArH^{2-},$$
$$2ArH_2^- \rightarrow ArH_3^- + ArH^-.$$

The stable AR can also detach a proton from extremely weak acids, entering into the role of effective metallating agents[67,167,173]. Thus Normant and Angelo[67] used naphthalenesodium for the metallation of carboxylic acids and their salts. The yields of the corresponding malonic acids (after carboxylation) reached 80%.

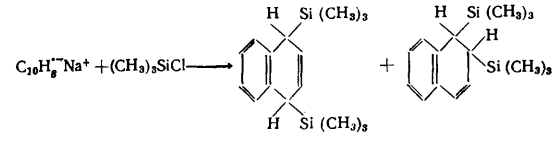
The carboxylation of AR, like hydrolysis, leads to the formation of dihydro-derivatives of the initial aromatic hydrocarbons[168,169]. For example, a mixture of 1,2- and 1,4-dihydronaphthalenedicarboxylic acids is obtained from the AR of naphthalene:



Unlike the reactions of aromatic AR with alkyl halides considered in the previous section, the reaction of dimethyl sulphate with the AR of biphenyl leads to the formation of a dimethylated product[170]:

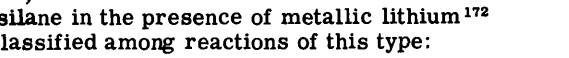


Chlorotrimethylsilane reacts similarly with the AR of naphthalene[171]:



1,2- and 1,4-isomers are formed in the approximate ratio of 1 : 2.

Evidently, the formation of bis-3,6-(trimethylsilyl)-cyclohexa-1,4-diene in the reaction of benzene with chlorotrimethylsilane in the presence of metallic lithium[172] must be classified among reactions of this type:



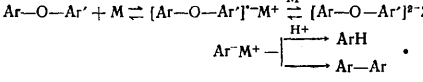
The reactions with toluene and anisole proceed similarly.

IV. REACTIONS WHICH PROCEED THROUGH THE INTERMEDIATE FORMATION OF RADICAL-IONS

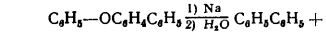
The development of physicochemical methods of investigation, and above all of EPR, gave the possibility of tracing the formation, and in some instances also the kinetics, of the accumulation and decomposition of short-lived AR during chemical reactions. The results obtained are undoubtedly of considerable interest in themselves but in addition they clearly show the large part which electron transfer processes play in various chemical changes.

1. Cleavage of Carbon–Element Bonds

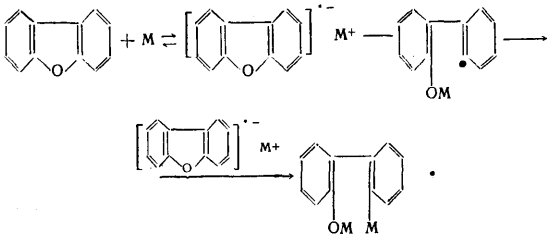
The cleavage of diaryl and alkyl aryl ethers by alkali metals has long been known[174] and in some instances finds synthetic application for the production of compounds containing a free hydroxyl group, but the mechanism of this process has still not been established. Recently, Eargle[175] and Strojny[176] showed that the first act of the reaction is the transfer of an electron from the alkali metal atom to the ether molecule with the formation of an AR; the latter takes a second electron, forming a dianion, the decomposition of which also leads to the products of the reaction:



The direction of the splitting of the dianion into different Ar and Ar′ depends on the nature of the aromatic radical[176]. For example, with biphenylyl phenyl ether, phenol and biphenyl are formed:

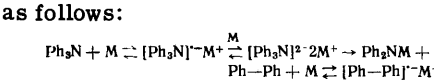


It is interesting to note that dinitrodiphenyl ether does not cleave under the conditions of the experiment[175]. This is evidently due to the delocalisation of an unpaired electron on the nitrogen atoms of the nitro-groups, which leads to the decrease in the electron density on the oxygen atom. The splitting of the C–O bond in dibenzofuran takes place at the AR stage. The radical formed as a result of the breaking of the bond is rapidly reduced by another molecule of AR into the corresponding anion[177]:



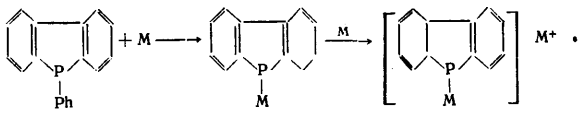
The kinetics of the decomposition of the AR was measured from the change in the intensity of the EPR signal. The activation energy depends slightly on the nature of the metal (19.0 kcal mole^{-1}). Splitting with alkali metals and other heterocyclic compounds evidently proceeds in a similar manner.

In investigating the splitting of compounds of the type Ar_3E (where E = N or P) by alkali metals the formation of a primary AR of the type $[Ar_3E]^-M^+$ has not yet been established (see Eliseeva and coworkers[35]). Thus with triphenylamine the only identifiable paramagnetic product is the AR of biphenyl[178]. The probable scheme of the decomposition, as for the diaryl ethers, can be represented as follows:



The splitting of triphenylphosphine[33] stops at the first stage with the formation of Ph_2PM, which is reduced by an excess of the metal to the dianion radical $[Ph_2PM]^{\cdot-}M^+$.

Biphenylylene(phenyl)phosphine [9-phenyl-9-phosphafluorene] reacts similarly with alkali metals[34]:



The metallation of aromatic hydrocarbons containing "acid" hydrogen atoms also proceeds through the stage of formation of AR.[179-181] It has been shown, by the example of indene and fluorene, that the AR formed can either decompose with the loss of a hydrogen atom, or detach a proton from a neutral molecule:

$$ArH + M \rightleftarrows ArH^{\cdot-}M^{+}$$

$$ArH^{\cdot-}M^{+} \rightarrow ArM + H^{\cdot}$$

$$ArH^{\cdot-}M^{+} + ArH \rightarrow ArM + ArH_{\text{a}}^{\cdot} .$$

Which direction predominates depends on the nature of the initial hydrocarbon and the alkali metal. A unimolecular decomposition is catalysed by iron(II) salts[180].

Evidently, just the same happens in the breaking of the N–H bond. Thus, in the action of metallic potassium on carbazole in a medium of dimethoxyethane at low temperature the formation of an AR was established[182]; it was converted on heating into carbazylpotassium with the liberation of hydrogen. Solutions of the alkali metals in amines also slowly liberate hydrogen, forming the corresponding amides. It is interesting to note, that as for the AR of fluorene, this decomposition is accelerated by iron(II) ions.

Summarising all that has been said above, the general conclusion can be drawn that reactions with free metals start with the transfer of an unpaired electron to a molecule of another reagent with the formation of an AR, the subsequent conversion of which also determines the occurrence of the process as a whole.

This general position can, we consider, be extended also to one of the main reactions of organometallic chemistry—the reaction of metals with halogen derivatives, leading to the formation of a metal–carbon bond. Although this reaction was discovered more than a century ago, the mechanism of the process cannot be considered to be explained. Each of the suggested approaches to the solution of this problem is confirmed by the indirect evidence, but in not one instance is the reasoning conclusive.

Any scheme which pretends to give a rather complete explanation of the nature of this reaction should successfully explain not only the very fact of the formation of a metal–carbon bond but also the nature of the side processes, the effect of the solvent, stereochemical features of the synthesis, etc.

All the points of view on this subject can be roughly divided into two large groups, depending on which of the two species—the radical $R^{\cdot}$ or the carbanion R^{-}—is ascribed the part of "actual start" in the intermediate stage of the reaction.

Suggestions about the free radical nature of the reaction are based mainly on the studies of Polyani and coworkers[183,184], completed as long ago as 1930. The authors studied the reaction of sodium vapour with methyl halides. A kinetically bimolecular reaction leads to the formation of free methyl radicals identified by their reaction with iodine vapour:

$$CH_3X + Na \rightarrow Na^{+}X^{-} + {}^{\cdot}CH_3 .$$

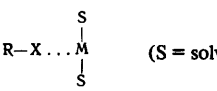
The activation energies fall sharply with decrease in the strength of C–X in the order F $\gg$ Cl > Br > I.

It is claimed that in a transition state of type $\geq C \ldots X \ldots M$ transfer of an electron takes place from a metal atom to a chlorine atom, which leads to the production of an ion pair $M^{+}X^{-}$ which is removed from the free radical formed simultaneously.

On the other hand, even from the work of Paneth it is well known that free radicals are readily "seated" on the free valencies of the metal with the formation of organometallic compounds[185,186]. Even a simple comparison of these two factors leads to the hypothesis of the free radical nature of the whole process: in the adsorbed layer on the metal surface (according to Polyani's scheme) free radicals are generated, which, by reacting with this surface, also form metal–carbon bonds. In this instance when the chemisorption is insufficient the possibility appears of the escape of the free radicals into the solution with all the consequences that follow: recombination (dimeric products, R–R), disproportionation (mixture of hydrocarbons RH and R_{-H}), interaction with the medium (hydrocarbons RH). On the basis of the extremely approximate kinetic results about the reaction of magnesium with alkyl halides[187,188] even the assumption about a radical-chain mechanism was advanced, which agrees with the existence of an induction period, the acceleration of certain reactions when irradiated, etc.

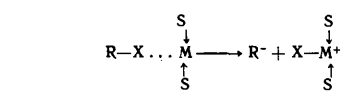
Another viewpoint mainly being developed by the French school (Prevost[189], Normant[190], and others) is that during the course of organometallic synthesis a carbonion R^{-} is formed as the active species.

In this instance the reaction of an alkyl halide with a metal is regarded as the nucleophilic attack of the metal due to the unshared electron pairs of the halogen. In Prevost's opinion[189], such interaction cannot by itself lead to the formation of a carbanion without the participation of an outside donor of electrons, which is the solvent. The common attack of the halogen and solvent leads to the removal of a metal atom from the lattice and the formation of a hypothetical species of the type:



(S = solvent, M = divalent metal)

which then undergoes intramolecular electron transfer:



The carbanion which is formed either adds to a positively charged metal atom (normal reaction), or participates in the formation of side products:

$$R^{-} + RX \rightarrow R{-}R + X^{-}$$

$$R^{-} + RX \rightarrow RH + R_{-H} + X^{-} .$$

It would appear that a single answer about the validity of one or another of the schemes given above can be given by a study of the stereochemistry of the replacement of a halogen connected to an asymmetric carbon atom by a metal. However, the available results on this seem contradictory. Moreover, the interpretation of any stereochemical results is hindered in this instance by the impossibility of the unambiguous assignment of this reaction to any of the accepted types of substitution. The stereochemistry of redox substitutions has not yet been studied systematically and a basis for the prediction of the stereochemical results of such reactions is still impossible.

The available facts lead to the following results. The stereoisomeric *cis-trans*-halides of the propenyl and stilbenyl types react with lithium, almost completely retaining

the configuration of the sp^2-carbon atom, which is also retained in subsequent reactions for the transfer of an unsaturated radical[191,192].

The stereochemical "purity" of the reaction of *trans*-β-bromostyrene with magnesium depends somewhat on the solvent[193]; however, here also it is possible to speak about retention of configuration.

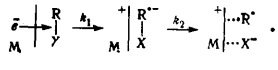
The substitution of a metal for a halogen connected to a saturated sp^3-carbon atom is less stereospecific on the whole. Optically active organo-magnesium[195] and -lithium[194] compounds are obtained from (+)-(*S*)-1-halogeno-1-methyl-2,2-diphenylcyclopropane; however, most optically active halides of the type RR'R"CX,[196] for example, (−)-3,3-dimethylcyclohexyl chloride[197], form racemic organometallic compounds.

In the reaction of a series of optically active halides with metallic sodium (Wurtz reaction) the optical activity is partly retained[198].

Strictly speaking, all these results do not prove and do not rule out any of the proposed schemes. In particular the retention of the configuration can result both from the formation of "intimate radical pairs" of the

type, where there is no free rotation[194] and from the similarly constructed ion pairs formed by the carbanion and metal ion which are produced.

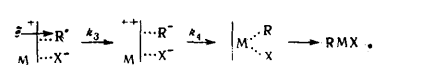
It should be borne in mind that the two main approaches to understanding the mechanism of the RX + M reactions are not mutually exclusive. In any case the first act of this redox reaction taking place on the metal surface must be considered the transfer of "dead" electrons of the metal lattice to the adsorbed molecule of halogen and the formation of the corresponding AR§, $RX^{\cdot -}$,[199] after which there is the breaking of the C–Hal bond and the formation of an organic radical and a halide anion adsorbed on the metal surface:



Depending on the nature of the metal, the organic halide, and the solvent, the breaking of the C–Hal bond can also proceed synchronously with the electron transfer ($k_2 > k_1$). In the last instance the elementary act can be regarded as the nucleophilic attack on the halide adsorbed on the metal surface by an electron (type S_N2)

$$\bar{e} + RX \longrightarrow \bar{e} \ldots R^{\delta+} \ldots X^{\delta-} \longrightarrow R^{\cdot} + X^{-}.$$

The radical which has been formed takes a second electron, being converted into a carbanion, and simultaneously the metal cation enters the solution:



The medium has an enormous influence on the occurrence of all the stages of this process. Firstly, the solvent facilitates the transfer of the electron both on account of the solvation of the cationic centres on the metal and also owing to its own affinity for an electron, which makes possible the transfer of an electron from the metal to the halogen through the solvent¶. Secondly, donor solvents facilitate the stabilisation of AR, $RX^{\cdot -}$, and finally they facilitate, owing to the solvation, the escape of a metal cation into the solution. Catalytic additions evidently usually act similarly.

As regards the mechanism of formation of the side-products (R–R, RH, R_{-H}), two completely different processes must be distinguished: the formation of side-products during the synthesis of an organometallic compound and their formation due to secondary reactions of the metal alkyl already formed. The second type of reaction will be considered in the section dealing with substitutions.

If the rate of conversion of a radical R' into a carbanion is low in comparison with its rate of formation (k_1 and $k_2 > k_3$), there is some probability of its recombination with another of the same radicals on the metal surface (formation of R–R hydrocarbon) or of its escape into the solution (hydrocarbons RH and R_{-H}). A certain amount of side-products can arise due to the reaction of the described carbonium ion R^- with the solvent or form an excess of unreacted halogen derivative:

$$R^- + H^+ \quad \text{(from solvent)} \longrightarrow RH$$
$$R^- + RX \longrightarrow R{-}R + RH + R_{-H} + X^-.$$

If the rate of addition of the second electron is greater than the rate of splitting of the C–Hal–($k_3 > k_2$), the carbanion formed should retain the geometric configuration of the initial halogen derivative. Naturally, this condition can be fulfilled for the more active metals and halogen derivatives, the molecules of which contain atoms and groups of atoms capable of delocalisation of the unpaired electron in RX^-. Actually, optically active organometallic compounds of lithium and magnesium could be obtained only from (+)-(*S*)-1-halogeno-1-methyl-2,2-diphenylcyclopropane, and in the formation of the organomagnesium compound the degree of racemisation is significantly greater[194,195].

If the metal taking part in the reaction is incapable of forming a normal organometallic compound the process stops at the stage of formation of a radical which subsequently either dimerises or disproportionates. Such a direction of the reaction is brought about by the reaction of halogen derivatives with metal derivatives[200].

2. Substitutions

The ability of the anions to act as active electron donors suggests that in many instances the reaction of anions proceeds in stages, the first stage being the transfer of an electron from the anion to the acceptor. Indirect confirmation of this hypothesis is the linear relation between the rate of reaction of the anion (nucleophilic nature) and the half-wave oxidation potential[201–203].

Let us consider, for example, the reaction of anion A^- and cation B^+. Because of the difference in electron affinity of A^- and B^+ (which is completely natural on taking into account that in many reactions the anions act as donors and the cations as acceptors of electrons), the first act is the transfer of an electron from anion to cation with the formation of two radicals, the recombination of which leads to a product corresponding to the normal heterolytic process:

$$A^- + B^+ \xrightarrow{k_1} A^{\cdot} + B^{\cdot} \xrightarrow{k_2} A{-}B.$$

The recombination and disproportionation of like radicals and their interaction with the medium leads to the formation of side-products. Since the recombination of radicals (k_2) usually proceeds at an extremely high rate the observation of valence-unsaturated intermediate species is

§ For the principal possibility of the existence of AR of this type, see p.956.

¶ This assumption is based on the solubility of a series of active metals in amines, esters, and other aprotic solvents[49–54].

possible only when there is a rather large difference in the electron affinities of the initial reagents, that is, when the rate of electron transfer is rather high and is not the rate-limiting stage of the process ($k_1 > k_2$).

In some instances only one of the radicals can be observed (A˙ or B˙) which exhibits relative stability, when the second radical similarly simultaneously participates in some side-process. Finally, there can be the example when the radicals formed are incapable of further changes, that is, the reaction stops at the stage of electron transfer.

Similar discussions can also be held for the reactions of anions (and cations) with neutral molecules (reactions of the ion–dipole type) and for reactions between neutral molecules (reactions of the dipole–dipole type). In the last example the complete transfer of an electron evidently takes place relatively rarely in media of high solvating ability. In many instances some displacement of the electron density takes place with formation of a charge-transfer complex (CTC)†.

Evidently the first experimental confirmation of the formation of radical species in reactions between neutral molecules was obtained in 1958 [7] in an EPR study of the reaction of chlorotriphenylmethane with ethyl-lithium. The concentration of the triphenylmethyl radical under the conditions of the experiment considerably exceeded the equilibrium value which was convincing proof of its primary nature:

$$Ph_3CCl + EtLi \longrightarrow Ph_3C^{\cdot} + LiCl + Et^{\cdot},$$
$$2\,Ph_3C^{\cdot} \longrightarrow Ph_3CCPh_3\ .$$

In addition the results obtained did not solve the problem of the participation of the triphenyl radical in the normal substitution since the reaction products were not studied.

In investigating the reaction of benzophenone with various alkyl- and aryl-magnesium halides the formation of benzophenone ketyl was observed[76]. However, in this instance the results obtained did not permit a definite conclusion to be drawn about the role of electron transfer in normal additions.

In studying the reactions of *p*-nitrobenzyl chloride and *p*-nitrocumyl chloride with various anions (the anion of 2-nitropropane, 2-ethoxycarbonylcoumaran-3-one, the thiophenolate ion), Kornblum and coworkers[205–208] noted the formation of paramagnetic species, which, in their opinion, are the AR of *p*-nitrobenzyl chloride or *p*-nitrocumyl chloride. However, since the authors did not obtain a resolved EPR spectrum, this assumption also cannot be considered completely proved.

Nevertheless, this assumption is indirectly confirmed by the fact that the substitution is retarded by *p*-dinitrobenzene and molecular oxygen.

The present authors with Bubnov recently showed that the alcoholysis of triphenylmethyl chloride and perchlorate with potassium t-butoxide proceeds through a stage of electron transfer[209]. On mixing solutions of triphenylmethyl chloride (or triphenylmethyl perchlorate) with a solution of potassium t-butoxide in the microwave cavity of an EPR spectrometer a well resolved signal of the triphenylmethyl radical was observed, the concentration of which passes through a maximum during the course of the reaction. If potassium 2,4,6-tri-t-butylphenoxide is taken instead of potassium t-butoxide, the reaction stops at the stage of single-electron transfer, since the triphenylmethyl and 2,4,6-tri-t-butylphenoxyl radicals which are formed do not recombine with one another. Measurement of the concentration of phenoxyl radical shows that this process takes place quantitatively. These results show that the classical, as it were, S_N1 reaction is in reality at least a two-stage process: electron transfer and the subsequent recombination of two radicals.

Electron transfer processes evidently also play an important part in nucleophilic substitutions in the aromatic series. It was shown recently[210] that the reaction of esters of *p*-nitrophenol with alkoxides take place through the formation of the corresponding AR.

Despite the fact that electron transfer in substitutions has at present been proved only in isolated instances we consider that this process is extremely general and the lack of direct experimental confirmation is determined by technical difficulties.

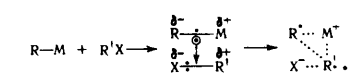
One of the main reactions of organometallic chemistry approaches very closely to the reactions considered: the reaction of organometallic compounds with halogen derivatives. This reaction usually proceeds ambiguously and leads to a complex mixture of products. At least two main directions can be distinguished for this process: double decomposition leading to the formation of a new organo-elemental compound and a halogen derivative.

$$RM + R'X \rightarrow R'M + RX$$

and the Wurtz reaction:

$$RM + R'X \rightarrow R{-}R' + MX\ .$$

The latter is usually complicated by a series of side processes leading to the formation of hydrocarbons of the type RR, R′R′, RH, R_{-H}, R′H, and R'_{-H}. If the Wurtz reaction can be considered as a heterolytic substitution, the exchange reaction cannot be classified as any single type of reaction in accordance with the classification accepted in organic chemistry. Formally, during the course of the reaction there is a conversion of the "carbanion" of the organometallic compound into a "carbonium ion" of the halogen derivative and respectively the "carbonium ion" of the initial halogen derivative into the corresponding "carbanion". Hence it is quite evident that here we are dealing with a redox process. Since in this pair of reagents the donor properties should naturally be exhibited by organometallic compounds (RM), the first act of the reaction should be the transfer of an electron by the metal–carbon bond to the molecule of the halogen derivative:



In the complex which is formed two main directions of the process are subsequently possible: the transfer of a second electron with the formation of a carbanion R′⁻ (exchange reaction) and recombination of the radicals R˙ and R′˙, leading to the products of the Wurtz reaction. As well as these normal processes there is a certain probability of escape of radicals into the solution, which should lead to the formation of side-products—hydrocarbons of the type RH and R_{-H}. Since as a result of the exchange reaction both organometallic compounds (initial and that formed from the added halogen derivative) are always present in the reaction mixture, their reactions with the halides leads to the formation of the so-called "doubled" radicals—RR and R′R′. The ratio of the reaction products in each particular instance depends chiefly on the polarity of the C–M bond, the relative electron affinity of R˙ and R′˙, and the solvating ability of the medium. The higher the polarity of the C–M bond, the easier the electron transfer and the easier the normal reactions (compare the

† See Kosover[204] for the role of CTC in organic reactions.

organolithium and organomagnesium compounds). An increase in the difference in electron affinity of R and R′ facilitates the exchange reaction[211] and simultaneously can lead to a decrease in the yield of the product of the normal Wurtz reaction, if the organometallic compound formed reacts more readily with the initial halogen derivatives[212]. The role of the medium appears, on the one hand, in a change in polarity of the C–M bond and on the other in the solvation of the intermediate reaction complex. The stabilisation of this complex in solvating solvents should lead to an increase in the normal Wurtz and exchange reactions. Actually, many examples[212–214] have shown that a solvating solvent greatly facilitates a Wurtz reaction, whereas homolytic processes predominate in non-solvating media[215,216]. An increase in the solvating ability of the medium leads to a sharp increase in the exchange rate in the series of organolithium[218] and organomagnesium[219] compounds.

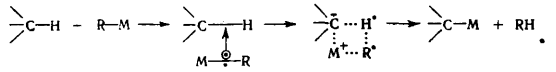
The problem of the catalytic activity of transition metal salts in this reaction is closely connected with the problem under consideration[220]. The role of these catalysts is that they serve as electron transporters, acting as an electron acceptor in relation to the potential carbanion of the organometallic compound. The reduced form of the catalyst then gives the excess electron to a molecule of the organic halide, and evidently such a stepwise electron transfer is hypothetical.

The first stage of this process is effected in the oxidative dimerisation of monosubstituted acetylenes by copper(II) ions in the presence of bases[217]:

$$RC{\equiv}C^- + Cu^{2+} \rightarrow RC{\equiv}C^{\cdot} + Cu^+$$
$$2\,RC{\equiv}C^{\cdot} \rightarrow RC{\equiv}C{-}C{\equiv}CR\,.$$

Depending on the nature of the initial reagents and catalyst this transfer can be effected either in a molecular complex[221,222] or both stages can proceed separately, so that the interaction of unlike radicals is hindered or completely impossible, as, for example, occurs in the reaction of alkylmagnesium halides with aryl halides[220]. In this connection it is not surprising that this reaction is catalysed also by certain other electron acceptors, for example, azobenzene[223].

General considerations concerning the mechanism of the RM + RX′ reaction can also be applied to the reactions in the metallation of aromatic hydrocarbons containing "acid" hydrogen atoms. In the reaction complex formed as a result of electron transfer the loss of a hydrogen atom takes place owing to its recombination with a radical from the organometallic compound:

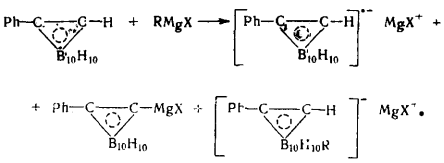


If the AR formed is relatively stable the radical from the organometallic compound can be attached to the aromatic system with formation of the corresponding alkyl derivatives. Actually, in several instances the alkylation of aromatic hydrocarbons under the action of organometallic compounds was observed. Thus in the metallation of perylene, in addition to perylenecarboxylic acid (after carboxylation) 13% 1-butylperylene and a little 3-butylperylene were isolated[224].

Dixon and coworkers[225,226] found that the ease of alkylation increases in the order toluene < benzene < biphenyl < < naphthalene, phenanthrene, but the electron affinity and ability to form AR increase in the same order[41,42]. The ease of alkylation of various organolithium compounds increases in the order n-BuLi < s-BuLi < t-BuLi and as already mentioned above, the ability of the RLi to transfer an electron increases in the same order[91].

A comparison of different RLi by their metallating ability in relation to triphenylmethane[227] and by their donor activity[73] leads to the same sequence: benzyl > allyl > > n-butyl > phenyl > methyl.

The formation of AR, alkylation, and metallation was observed in the reaction of phenylbarene with alkylmagnesium halides[228]:



Of course, it is impossible to regard the examples given as proof of the general scheme of metallation suggested, but the good qualitative agreement with the results of the experiments is indirect evidence in support of the above approach to the mechanism of metallation.

3. Other Reactions

First of all among the electron transfer reactions should be put the oxidation of organic compounds, but the number of experimental studies confirming this viewpoint are extremely few.

Russel and coworkers[229], in studying the oxidation of carbanions by oxygen, concluded that this reaction best agrees with the electron transfer scheme:

$$R^- + O_2 \rightarrow R^{\cdot} + O_2^{\cdot-}.$$

Several articles by Dewar and coworkers[230–232] on the oxidation of various aromatic esters by manganese(III) acetate appeared recently. The kinetic results suggest that in the systems studied the oxidation proceeds through a reversible stage of an single-electron transfer. Analogous results were obtained in investigating the kinetics of the oxidation of a series of the simplest amines by chlorine dioxide[233].

Direct experimental confirmation of electron transfer during oxidation was obtained by Smentowski[234], who observed the formation of AR by nitrobenzene in the oxidation of thiophenoxides by nitrobenzene:

$$ArS^- + PhNO \rightarrow \underset{\downarrow}{ArS^{\cdot}} + PhNO^{\cdot-} \rightarrow \text{reduction products}\,.$$
$$ArSSAr$$

Maruyama[235] noted the formation of diphenylnitrogen oxide in the reaction of phenylmagnesium bromide with nitrobenzene. Evidently in the reaction the diphenylhydroxylaminium anion formed is oxidised by the excess of nitrobenzene:

$$PhNO + PhMgX \rightarrow Ph_2NOMgX \xrightarrow{PhNO} Ph_2N{-}O^{\cdot} + PhNO^{\cdot-}.$$

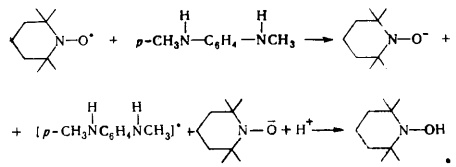
Similarly, the formation of di-t-butyl-[236] and t-butylphenylnitrogen oxide[237] probably occurs in the reaction of t-nitrobutane with t-butylmagnesium chloride and phenylmagnesium bromide.

The formation of the CR of tetramethylhydrazine was noted in the reaction of tetramethyltetrazine with various anhydrides of carboxylic acids[238]:

$$(CH_3)_2NN{=}NN(CH_3)_2 \xrightarrow[0^\circ]{Ac_2O} N_2 + [(CH_3)_2NN(CH_3)_2]^{\cdot+}.$$

Interesting results were obtained in investigating the reaction of stable nitrosyl radicals with aromatic amines.

It was found that the formation of hydroxylamine is a two-stage process: electron transfer from the aromatic amine and addition of a proton from the solvent[239]. In this the aromatic amine is converted into the corresponding CR:



Finally, there are results on the important role of electron transfer reactions in the isomerisation of tetraphenylbutadiene[240], Friedel–Crafts alkylation[241], the diene synthesis[242], and several other processes.

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The subject under discussion is extremely general in character since it evidently touches all the fields of organic chemistry to some extent. Therefore an exhaustive treatment of single-electron transfer reactions would scarcely be possible within the framework of a single review.

Nevertheless the material presented shows that electron transfer reactions play an important part in the elementary acts of many organic reactions. The transference ideas about the electron, both about the kinetic particle widely distributed in inorganic and radiation chemistry, into organic chemistry allows the mechanism of organic reactions which do not fit within the framework of classical theory to be explained in many instances (for example, it allows the simultaneous occurrence of homolytic and heterolytic processes to be explained from a single standpoint).

The fruitfulness of such an approach is also confirmed by the fact that the number of publications devoted to electron transfer reactions in organic chemistry has grown sharply recently. The further accumulation of experimental results in this field will undoubtedly lead to an extension of our knowledge about the nature of chemical changes.

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Stereospecific Catalysis in the Field of Optically Active Polymers

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The present review examines a new field of polymerisation catalysis—the catalytic synthesis of optically active polymers of various classes: (1) poly-α-alkenes under the influence of dissymmetric catalysts, acting as anionic or cationic catalysts, and (2) poly-oxides and poly-imines under the influence of both heterogeneous and homogeneous coordination catalysts. The stereospecific polymerisation of optically active alkenes and the stereoselective polymerisation of racemic alkenes using optically active catalysts are examined. The bibliography contains 127 references.

CONTENTS

I.	Introduction	969
II.	The role of heterogeneous catalysts in stereospecific polymerisation	969
III.	Dissymmetric polymerisation catalysts	970
IV.	The stereoselective polymerisation of optically active α-alkenes	973
V.	Stereospecific catalysis in the polymerisation of propene oxide and imines	975
VI.	The stereo-elective polymerisation of DL-propene oxide under the influence of dissymmetric catalysts	976
VII.	The stereo-elective polymerisation of DL-α-alkenes	980

I. INTRODUCTION

Progress in stereospecific catalysis has been particularly extensive in the field of optically active polymer synthesis. In recent years, fundamentally new stereoselective and stereo-elective processes have been carried out, and the advantages of the use of optically active compounds in the study of the mechanism of stereospecific catalysis have been demonstrated. Work has also begun on the directed synthesis of optically active polymers with required structure for use as dissymmetric adsorbents and catalyst components[1,2].

The present review is restricted to an examination of the conditions of the catalytic synthesis of optically active polymers, the part played by heterogeneous dissymmetric catalysts in the stereospecific polymerisation of α-alkenes, propene oxide, and imines, and the catalytic stereo-elective polymerisation of propene oxide and poly-α-alkenes.

The large amount of experimental material examined in the present review has been obtained chiefly by Natta, Furukawa, Tsuruta, and their schools, and demonstrates convincingly the part played by asymmetric adsorption and complex formation in asymmetric polymerisation catalysis; this is of considerable interest for an understanding of the mechanism of heterogeneous and homogeneous dissymmetric catalyst action.

II. THE ROLE OF HETEROGENEOUS CATALYSTS IN STEREOSPECIFIC POLYMERISATION

The presence of the surface of a heterogeneous catalyst in a reacting system decreases the number of symmetry elements compared with a homogeneous reaction, so that we should expect the production of greater stereoregularity in the polymerisation products in the presence of heterogeneous catalysts. Stereoregular polymers may also be formed, however, in homogeneous radical polymerisation under certain conditions.

Heterogeneity of the catalytic system, which is essential for the preparation of stereoregular poly-α-alkenes, apparently becomes superfluous in the polymerisation of other monomers (aldehydes, dienes, and acrylates). According to Schildknecht[3], stereoregular poly(vinyl isobutyl ether) may also be formed in the absence of a solid surface with soluble catalysts[4]. In this instance, however, the structure of the monomer and the conditions of polymerisation are of particular importance. The monomers should contain not less than two functional groups interacting electronically with one another, the reaction must be carried out at low temperatures to reduce the freedom of rotation of the chains, and the presence of large bulky groups in the monomer leads to rigidity of the chains and high stereoregularity[5]. Since stereospecificity is determined by the atomic configuration surrounding the ends of the chain and situated not more than 20 Å from it, and since this corresponds to the dimensions of large complexes, the production of stereospecificity, according to Szwarc and Smid[6], requires the presence of a macroscopic surface. Thus isotactic polystyrene can also be obtained in homogeneous solution with $n\text{-}C_4H_9Li$ as initiator at −30°C. The solvent also has a considerable influence: in toluene, methyl methacrylate gives an isotactic polymer with a fluorenyllithium catalyst, but a syndiotactic polymer in dimethoxyethane. If we ignore particular instances, however, heterogeneity of the system remains a necessary condition (particularly in the polymerisation of α-alkenes) for the production of stereoregular polymers. With heterogeneous catalysts, stereospecificity depends to a significant extent on the stage involving adsorption of the monomers at the active centre on the solid catalyst surface. Stereoregular polymers are obtained on catalysts acting by an ion-coordination mechanism (anionic and cationic). These contain metals capable of coordinating molecules of the monomer before the stage corresponding to their introduction into the growing chain. A specific action is shown by metals with small ionic radius (Al, Be, and Li) and compounds of the transition metals. The steric effect of bulky groups in the coordinating monomer is also significant. This factor cannot be decisive in stereospecific polymerisation, however, and it can lead only to stereoregularity of the syndiotactic type.

Different authors have different views on the mechanism of Ziegler–Natta catalyst action (see Tsuruta's monograph[7]), but in one respect they agree: the structure of the macromolecule is determined by the stage in which the monomer is adsorbed on the surface of the heterogeneous catalyst. The active centre on the surface may contain metal alkyls adsorbed on $TiCl_3$ or $TiCl_2$ (Friedlander), and the mechanism of chain growth is a form of matrix polymerisation, when both ends of the chain are attached to the surface. According to Nenitzescu, the organotitanium compounds, which undergo splitting to form radicals, act as the catalyst. Natta considers that in coordination anionic polymerisation, adsorption of AlR_3 takes place on the surface of the $TiCl_3$ crystals with the formation of active centres, the number of which can be determined, for example, by using AlR_3 labelled with ^{14}C.

Asymmetric centres are formed with the participation of aluminium atoms and the spatial configuration of the chain is determined by the way in which the monomer molecule approaches between Al and R. Since two approaches are possible, the resulting polymer (isotactic) consists of a mixture of DDD- and LLL-structures.

When two of the coordinating groups are of different chemical character, enantiomorphic structures are possible in the surface complexes. High stereospecificity in such a catalyst should be produced when it is joined to a growing chain (Natta[4]).

The problem of the nature of the active centres has been the subject of detailed discussion. According to the data of Carrick and coworkers[8], and contrary to Natta's opinion, growth takes place at transition metal active centres without direct participation of the reducing agent (AlR_3). Cossee[9] suggests that polymerisation takes place at a titanium ion on the surface of the $TiCl_3$ (or $TiCl_2$) lattice, in which one of the chlorine atoms has been replaced by an alkyl group R, and beside which there is a vacant site on which adsorption of the monomer molecule takes place. After this stage, the Ti–Al bond and the vacant site are preserved in the active centre, and only their positions change.

Polymerisation by the anionic mechanism is influenced considerably by steric factors, because of the small radius of the coordinating metal cation. The stereoregulating power of these catalysts is greater than that in cationic polymerisation, and steric factors are decisive. It is considered that the monomer molecule being attached should be orientated beforehand, but the essential features of the transition state have not yet been determined.

According to Cossee[9], the active centre of heterogeneous Ziegler–Natta catalysts is a transition metal ion with octahedral configuration. When the α-alkene molecule is adsorbed on the surface, its position is such that it forms a π-bond with the titanium ion and occupies the vacant site in such a way that the CH_3 group (in the case of propene) is directed away from the surface, and the CH_2 group is directed towards the surface of the catalyst.

This orientation of the monomer molecule explains the "head-to-tail" addition. The action of AlR_3 reduces to alkylation of the catalyst surface. This scheme explains the formation of isotactic polymers and the fact that alkenes with a non-terminal double bond and with a large R group do not undergo polymerisation at all. Moreover, compounds such as acetylene, water, and CO act as poisons, since they are firmly bound to the catalyst on the vacant sites.

Cram[10] explains stereospecific polymerisation on the basis of steric repulsion between the substituents in the monomer and the penultimate link in the chain. The growing chain takes its origin from the edge of the catalyst crystal. The monomer entering the chain will react with least steric hindrance when R is on the same side as H— on an asymmetric carbon atom.

It is evident that we should expect a much greater part in this process to be played by a dissymmetric catalyst capable of forming surface diastereoisomers on asymmetric adsorption. Cossee's scheme readily explains the formation of these "diastereoisomers".

These ideas were used by Krylov and Livshits[11-13] to explain the asymmetrising action which they observed for the heterogeneous catalyst magnesium d-tartrate in the polymerisation of propene oxide.

Ideas about the existence of asymmetric centres on the catalyst surface were put forward in general form by Hartung and coworkers[14]. They examined various types of centre on the surface of a catalyst on the basis of Ogston's "three-point adsorption"[15] and Balandin's multiplet theory of catalysis[16].

If two enantiomorphic centres are present in different quantities, stereospecificity is not observed. In the examination of this problem, however, Hartung and coworkers[14] reached an incorrect conclusion by assuming that in the hydrogenation of, for example, (–)-α-oximinopropiophenone the optically active product is formed as a result of the action of only one type of centre[17], whereas this result is due to purely steric interaction as a consequence of asymmetric synthesis under the influence of the original asymmetric centre in the molecule.

To investigate the problem of the properties of the enantiomorphic complexes formed between the dissymmetric centres of the catalyst and the monomer molecule, it is convenient to use the approach proposed by Pajaro, Corradini, and coworkers[18,19], who studied diastereoisomeric complexes of alkenes with optically active complex compounds.

An alkene with unsymmetrical structure can be coordinated by means of a $\sigma\pi$-bond to a transition metal complex with the formation of two enantiomorphs. If the transition metal compound contains an optically active ligand, the diastereoisomers formed with the alkene may be separated. The complexes $PtCl_2$[(–)-(*S*)-α-phenylethylamine]X, where X = styrene, propene, *trans*-but-2-ene, or *cis*-but-2-ene, have in fact been prepared and separated. The following values of $[M]_D^{18}$ were obtained for the first three diastereoisomers: $+1200° \pm 150°$, $-300° \pm 50°$, and $-280° \pm 20°$ As expected, the complex with *cis*-but-2-ene did not give diastereoisomers, because of the symmetry of the molecule.

Asymmetric induction arises on coordination of an alkene to the surface of a heterogeneous catalyst in which asymmetric centres have been produced beforehand.

III. DISSYMMETRIC POLYMERISATION CATALYSTS

1. The Catalytic Asymmetric Synthesis of Poly-α-alkenes

The polymerisation of α-alkenes is the most widely studied field of stereospecific vinyl polymerisation. Isotactic poly-α-alkenes have been prepared only using heterogeneous catalysts, and high stereospecificity has been observed when the organometallic component has been deposited (according to Natta) on the carrier—crystalline modifications of $TiCl_3$, with a layer lattice. The use of other carriers, for example, β-$TiCl_3$, which has a different lattice, or metal oxides, gives polymers with low regularity.

We should expect a greater structural regularity in optically active polymers than in the corresponding polymers formed from their racemic monomers, since the presence of the asymmetric centres in the monomer, as a result of their steric influence, will facilitate the predominant formation of one chain configuration.

An incorrect understanding of the role of the asymmetry of the atoms in the polymer chain has led to attempts to prepare optically active vinyl poly-α-alkenes.

Murahashi and coworkers [20] polymerised styrene under the influence of a catalyst consisting of $TiCl_3$ + tri-(2-methylbutyl)aluminium at 70°C and obtained polystyrene which was identical with the polymer obtained with a racemic catalyst. The polymerisation of styrene with optically active 2-methylbutylsodium also gave an inactive polymer. Braun and Kern [21] found, however, that polystyrene obtained using the optically active 2-methylbutylsodium (optical purity 85%) exhibited slight rotation (up to 0.120°; $[\alpha]_D^{20}$ + 0.60°). Calculation of the contribution of the terminal groups to the polymer chain showed that the optical activity of the polymer does not exceed the values due to the formation of $C_5H_{11}-CH_2CH(C_6H_5)-$ groups at the ends of the chain. This contribution is greater for the amorphous fractions with low molecular weight, where the macromolecule contains one 2-methylbutyl group (0.120° for M = 5400) and is smaller for the isotactic fractions (0.011° for M = 28 800). The use of rotatory dispersion enabled larger rotations to be observed for amorphous polymers.

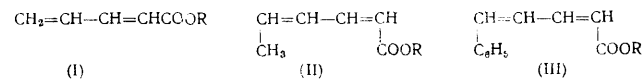
Thus, although in this example of heterogeneous catalysis we might expect steric control of the monomer orientation in the initiation stage at the catalyst surface, these results indicate that polymerisation begins with the alkyl anion of the catalyst.

Fray and Robinson [22] hoped to prove the presence of optical activity in polypropene obtained using (+)-tri(2-methylpentyl)aluminium (optical purity 38%), by subjecting the polymer to pyrolysis. It was expected that optical activity would appear in the chain fragments with low molecular weight, both as a result of the presence of asymmetric atoms and as a result of "spiralisation" of the chain. The results were negative, however.

It has been known for a long time (pp. 109 and 186 of Ref. 1) that an optically active solvent may have an asymmetrising action in the synthesis and separation of racemates. Theoretical examination of this problem by Amaya [23] showed that the probability of formation of optically active polymers under the influence of an optically active solvent increases with decrease in temperature and concentration. An attempt to induce "spiralisation" of the chain by polymerising propene using (+)-tri(2-methylpentyl)aluminium under the asymmetrising influence of (+)-pinane as solvent was unsuccessful, however [20].

Studies in the field of optically active poly-α-alkenes are associated chiefly with the names of Natta and Pino. Natta and coworkers [24] carried out the asymmetric catalytic synthesis of tritactic polymers from optically inactive monomers using dissymmetric catalysts. The dissymmetric catalyst 2-methylbutyl-lithium with methyl *trans-trans*-sorbate gave polymethyl sorbate [25] with $[\alpha]_D$ equal to −3.1° (α_D = −0.235°, *c* = 2.55, *l* = 3); $[M]_D$ = 3.9°; and $[M]_{375}$ = −13.5°. The original *trans-trans*-sorbate gives only *erythro*-di-iso-*trans*-tactic polymethyl sorbate. The other possibilities (*trans-threo*, *cis-threo*, and *cis-erythro*) are not realised. Its optical activity is much greater than that which might have been expected from the contribution of the terminal groups to the rotation and is close to the value for the model compound. It was proved by chemical methods [25,26] and by using ^{14}C that terminal groups from the catalyst are not present in the polymer. The comparatively low value of α indicates that there is no spiralisation of the chain, as was suggested for poly-α-alkenes, and is due entirely to the asymmetric atoms in the main chain.

Highly crystalline 1,4-*erythro*-di-iso-*trans*-tactic polymers exhibiting optical activity have been prepared from esters of vinylacrylic (I), sorbic (II), and styrylacrylic (III) acids:



(I) (II) (III)

Table 1 gives data on the optical rotation of polymers obtained by polymerisation of these esters with a catalyst containing an optically active group [(+)-2-methylbutyl-lithium] and also using the complex of butyl-lithium with the asymmetric Lewis base, (−)-menthyl ethyl ether.

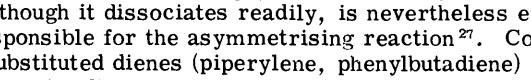
Table 1.

Monomer	Catalyst	Optical rotation of polymer in chloroform		$[M]_D$
		α_D, deg	$[\alpha]_D$, deg	
Methyl sorbate	(*R*)-2-methylbutyl-lithium	−0.70	−7.95	−10.0
Butyl sorbate		+0.36	+3.3	+5.5
Butyl β-styrylacrylate		+0.31	+2.0	+4.6
Methyl β-vinylacrylate	butyl-lithium-(−)-ethyl-menthyl ether		+7.2	
Methyl sorbate		0.27	+6.4	+3.0
Butyl sorbate		0.57	+8.4	+14.1
Butyl β-styrylacrylate		0.42	+3.7	+8.5

The mechanism of action of the first catalyst—the optically active organometallic compound R*Li—apparently involves the introduction of R* into the first monomeric unit, with subsequent transfer along the growing chain.

The second type of catalyst induces asymmetry in the first unit without the formation of a σ-bond between the dissymmetric agent in the catalyst and the chain.

When the catalyst $C_5H_{11}Li$ is used, the polymer contains one alkyl group for every 150–250 monomeric units, so that the optical activity cannot be due to their contribution to the total rotation (the value of $[\alpha]_D$ due to the terminal groups is smaller by a factor of 100 than the observed value of the rotation). Thus the optical rotation is due entirely to the asymmetric atoms in the chain. The same is true of the complex catalyst C_4H_9Li–menthyl ethyl ether, which, although it dissociates readily, is nevertheless entirely responsible for the asymmetrising reaction [27]. Conjugated substituted dienes (piperylene, phenylbutadiene) polymerise with dissymmetric catalysts to form optically active polymers with asymmetric centres in the main chain:



Starting from piperylene, Natta and coworkers [28] prepared *cis*-1,4-polypentadiene in which isotactic chains predominated. They used $AlR_3-Ti(OR)_4$ catalysts; in the system with R = (+)-2-methylbutyl and R = n-butyl, the polymer with high molecular weight did not show optical activity, and only the fraction with low molecular weight gave α_D = 0.03° ($[\alpha]_D$ = 1.76°), possibly due to the introduction of the terminal group from the catalyst.

The action of (+)-$Al(C_5H_{11})_3-VCl_3.(C_2H_5)_2O$ on *trans*-penta-1,3-diene [29] gives 1,3-*trans*-isotactic polypentadiene

with $[\alpha]_D = -1.05°$ ($\alpha_D^{18} = 0.11°$). The optical activity decreases with increase in molecular weight, indicating the occurrence of asymmetric induction in the initial stage of chain growth.

For the $Al(C_2H_5)_3$–(−)-tetra(menthoxy)titanium system, optically active *cis*-1,4-isotactic polypentadienes with maximal specific rotation of −22.8° and $[\eta] = 6.8$ (78% *cis*-chains) have been obtained.

This example is interesting since as well as optical activity due to the asymmetric atoms in the chain possibly there are also conformational factors: α increases with increase in the proportion of isotactic *cis*-1,4-structures. Moreover, the fact that an asymmetrising action is shown by a catalyst containing the asymmetric menthyl group joined to a titanium atom indicates that the transition metal is included in the active centre in the coordinating catalyst. The monomer is coordinated to this centre, and growth takes place on the surface of the heterogeneous catalyst.

Similarly, *trans*-pentadiene under the influence of the catalytic complex [VCl_3–(+)-tri-(2-methylbutyl)aluminium] gives optically active *trans*-1,4-isotactic polypentadiene[29].

Aliev[30,31] studied the asymmetric polymerisation of *trans*-1-phenylbuta-1,3-diene with (+)-2-methylbutyl-lithium and reported slight optical activity ($\alpha_D^{25} = 0.014$–$0.018°$ for $l = 1.55$), but this lies within the limits of experimental error. The use of rotatory dispersion did not permit a convincing demonstration of asymmetric synthesis, since although the value of $[\alpha]$ for $\lambda = 390$ nm increased by a factor of 2.5–3 compared with that for $\lambda = 589$ nm, the errors in the measurements showed a simultaneous increase, and this was not analysed.

Table 2.

Monomer/lithium ratio	Polyphenylbutadiene [η]	[α]390, deg	[α]390 M	Solvent	Monomer/lithium ratio	Polyphenylbutadiene [η]	[α]390, deg	[α]390 M	Solvent
37.6	0.075	+0.982	42.2	toluene	54	0.195	0.838	88.0	heptane
54	0.23	0.524	49.8	heptane	37.6	0.095	1.272	63.6	toluene
27	0.18	1.022	74.6	ditto	27	0.124	1.595	104	heptane

The polymerisation of phenylbutadiene on the complex catalyst butyl-lithium–(−)-menthyl ethyl ether at 0° and 15°C in heptane and toluene gave polymers with considerable activity and low characteristic viscosity (Table 2).

The highest optical activity in the polymers was observed at a ratio ether : butyl-lithium = 2. Decrease in the reaction temperature and increase in the solvent polarity lead to a decrease in the optical activity of the polymer. The optical rotation of the polymer specimens is independent of molecular weight, suggesting a mechanism of asymmetric growth, in which the asymmetric synthesis takes place as a result of the configurational orientation of the monomer on coordination to the lithium atom, through interaction with the asymmetric ligand—ethyl menthyl ether.

2. Asymmetric Cationic Polymerisation

In the polymerisation of cyclic monomers (benzofuran[32]), use is made of cationic catalysts, which form a complex with the optically active counter-ion, whose configuration determines, together with the growing chain, the spatial configuration of the first unit, and exercises steric control over chain growth. To intensify the stereospecificity of the action[23], the reaction is carried out between −75° and −100°C in toluene under the influence of, for example, the complex catalyst $C_2H_5AlCl_2$–(−)-β-phenylalanine (Table 3).

In each monomeric unit there are two asymmetric atoms; the polymer does not contain terminal groups from the catalyst, as proved by using phenylalanine labelled with ^{14}C.[33–36]

Table 3. Polymerisation of benzofuran on cationic catalysts.

Catalyst	Asymmetric co-catalyst	Polymer, $[\alpha]_D$, deg (benz.)	$[M]_D$, deg (diox.)	α_D
$AlCl_2 \cdot C_2H_5$	(−)-β-phenylalanine	−33.1	−39.1	−2.65
$AlCl_2 \cdot C_2H_5$	(+)-β-phenylalanine	+13.1	+15.5	
$AlCl_2 \cdot C_2H_5$	(+)-camphor-10-sulphonic acid	−3.8	−4.5	−0.68
$AlCl_2 \cdot C_2H_5$	(+)-tetramethylammonium camphor-10-sulphonate	−2.4	−2.8	
$AlCl_2 \cdot C_2H_5$	(−)-brucine	+2.8	+3.3	0.47
$AlCl_3$	(−)-phenylalanine	−28.5		

The polymer has a high conformational stability: it does not undergo racemisation even when heated in decalin at 200°C for several hours. This is also confirmed by the low temperature coefficient of optical rotation: $+0.04° \pm 0.01° \text{ deg}^{-1}$.

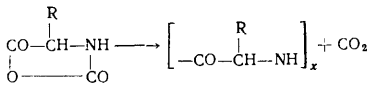
Although the optical activity is associated with the stereoregularity of the three-dimensional structure of the polymer chain, it does not necessarily lead to a tendency for the polymer to crystallise. Thus isotactic or di-isotactic polymers (for example, polybenzofuran) are obtained in amorphous form, although they are optically active. Sterically regular but amorphous polymers, for example, isotactic polymers, can be crystallised in the form of their derivatives, in which they retain their steric configuration: it is probable that, as for example in polybenzofuran, the steric conformation of the polybenzofuran chain is such that it does not permit regular packing of the chains in the crystal lattice[5,32]. It has been suggested that polybenzofuran is partly isotactic, since the optical activity in the main chain cannot be associated with a syndiotactic structure because of internal compensation. The optical activity of polybenzofuran remains constant with time. The rotatory dispersion curve shows a maximum at 303 nm: $[M]_{303} = -800°$.

The asymmetric synthesis is due to the orientating influence of the negative counter-ion situated on the growing end of the polymer chain. The efficiency of this asymmetric synthesis (calculated for unit linkage) is much greater than that for compounds with low molecular weight and approaches that of enzymatic asymmetric syntheses[33]. The mechanism, unlike that of the catalytic synthesis, evidently involves the transfer of asymmetric induction along the chain by means of the asymmetric counter-ion, the monomers being attached predominantly in one configuration. This mechanism is confirmed by the fact that the optical activity is independent of the molecular weight of the polymer[37,38].

Farina, Natta, and Bressan[38] established that the asymmetric polymerisation of benzofuran is autocatalytic. The optical activity depends to a marked extent on the monomer concentration, and from an initial value of 25–30° it passes

through a maximum in the course of the polymerisation, to a constant final value. If, at the start of the reaction, small quantities of previously formed or added polymer are already present, the value of $[\alpha]$ for the polybenzofuran formed is equal to the constant terminal value from the start of the reaction: $[\alpha]_D = 85-90°$. This suggests an autocatalytic reaction under the influence of the polymer formed. Three stages are observed in the polymerisation: (1) the formation of a polymer with low molecular weight and low value of $[\alpha]$, (2) increase in molecular weight and $[\alpha]$, and (3) new formation of fractions with low molecular weight. The second stage is autocatalytic[39]. In actual fact, the introduction of prepared polymer into the reaction sphere decreases the rate of the process by a factor of 5 to 10, but increases the asymmetrising effect, which is independent of both the sign and the magnitude of the rotation of the added polymer, and depends only on the asymmetry of the catalyst—the (+)-polymer is obtained using (+)-β-phenylalanine. The polymer formed probably intensifies the steric influence of the catalyst $AlCl_3$.(β-phenylalanine). Polybenzofuran, because of the presence of its oxygen atoms, can itself act as a Lewis base and modify the structure of the counter-ion. In the catalytic complex at a ratio $AlCl_3$: phenylalanine $\simeq$ 3, one mole of $AlCl_3$ is apparently held much less strongly, and the polymer formed produces a complex with $AlCl_3$, leading to modification of the catalyst. A polymer with high value of $[\alpha]$ is then formed under the influence of this catalyst. Thus as suggested by Natta and coworkers[38] the autocatalytic action is not steric but chemical in character.

This asymmetric autocatalysis shows a close analogy with enzymatic asymmetric syntheses in nature. A similar picture is also observed, for example, in the polymerisation of Leuch's anhydrides[40].



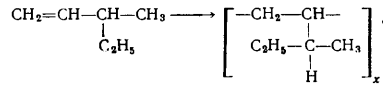
The kinetics of this reaction show a number of characteristic features: the rapid initiation stage is accompanied by chain growth processes which are at first slow (formation of a polypeptide with low molecular weight) and then rapid (conversion into a polypeptide with high molecular weight). According to Doty, a coil (β-peptide) is formed in the first stage, whereas in the second stage an α-spiral, which grows much more rapidly, is formed. If the reaction is initiated by an α-peptide, the first stage is not observed at all, but if the reaction is carried out in dimethylformamide, in which spirals are not formed, the second stage disappears. This mechanism is confirmed by study of the kinetics of the polymerisation of optically pure isomers of Leuch's anhydride and mixtures of the isomers. The homogeneous α-spiral is stable: the introduction of residues with opposite configuration decreases its stability. Thus the racemic mixture polymerises much more slowly than the optical isomer. The decrease in the rate of polymerisation of the latter when the antipode is added, however, is much greater than that when each isomer is polymerised separately. This is attributed to the fact that the polymerisation of, for example, the *d*-isomer, initiated by α-peptides obtained from the *l*-isomer, takes place slowly at first, and rapid polymerisation begins only when a sufficient number of *d*-units for the formation of a spiral are attached to the initiator. The role of the *d*-units (or other rigid conformations) can be seen from the fact that, for example, the addition of only 5% of the *d*-isomer to the *l*-anhydride is sufficient to decrease the rate constant by a factor of 3. The rate of polymerisation of the racemate is slower than that of the optical isomers by a factor of 17. Thus the polymerisation of the L-*N*-carboxyanhydride of γ-benzyl-L-glutamic acid takes place at a high rate when the polymer of γ-benzyl-L-glutamic acid is added as initiator. The reaction rate for the racemate of the anhydride is smaller by a factor of 2. In the system formed by the D-anhydride with L-polymer as initiator, the D-units are first introduced into the right-hand spiral of the L-polymer without altering its shape, but as the D-units accumulate, inversion of $[\alpha]$ is observed with an increase in rate as a result of the conversion of the α-spiral of the L-polymer into the left-hand spiral of the D-polymer.

Comparison of the relative rates of attachment of the D- and L-isomers to the right-hand α-spiral of the L-polymer showed that the L-anhydride is almost five times more active than the D-antipode[40].

IV. THE STEREOSELECTIVE POLYMERISATION OF OPTICALLY ACTIVE α-ALKENES

In the polymerisation of α-alkenes using an organometallic catalyst containing optically active alkyl groups[5] it was found that the active alkyl groups to some extent enter the polymer chain, and if the proportion of these groups is sufficiently large, optical rotation is observed in the low-molecular weight fractions. If optically active monomers are used as starting materials, however, the use of the same optically active catalyst leads to the formation of a polymer whose rotation may be 5–30 times greater than the optical rotation of the model compound, that is, a molecule with the structure of a unit in the polymer chain.

Bailey and Yates[41] at an American Chemical Society conference (1960) described a study of the effect of asymmetric atoms in the side groups of a poly-α-alkene on its crystallinity. The polymerisation of (+)-3-methylpentene ($[\alpha]_D^{25} = +33.49°$) with $TiCl_4$–$Al(n\text{-}C_4H_9)_3$ in xylene at 120–132°C for 7 days gave two polymer fractions: an atactic fraction with $[\alpha]_D^{23} = +94.9°$, and an isotactic fraction with $[\alpha]_D^{23} = -257°$ and m.p. 271–278°C, soluble only in 1,1-ditolylethane. (+)-3-Methylpentene with 4-methylpentene gave a copolymer with $[\alpha]_D^{26} = +112.4°$ and m.p. = 190°C, containing the monomers in the ratio 60 : 40. These authors attributed the marked increase in optical rotation in the polymer compared with the monomer to spiralisation of the chain



The polymer from *dl*-3-methylpentene had m.p. = 229–237°C, dissolved in 1,1-diphenylethane, and consisted of equal quantities of amorphous and crystalline phases.

An extensive series of papers on the polymerisation of optically active α-alkenes has been published by Pino and coworkers[42-55]. From optically active monomers they prepared optically active poly-α-alkenes with asymmetric centres in the side-chain. These reactions were carried out with ordinary Ziegler–Natta catalysts, and also with optically active organometallic catalysts. The latter were used to carry out stereo-elective polymerisation—selective polymerisation of one of the optical antipodes in a racemic monomer.

The polymerisation of α-alkenes on heterogeneous complex catalysts of the type $TiCl_4$–R_3Al gives polymers with a high degree of stereoregularity. A number of their characteristic properties led Pino and Natta to suggest that in the polymers, secondary structures of a spiral type,

similar to the α-spirals in proteins and polypeptides, are formed. The possibility that spiral structures are present in vinyl polymers was pointed out by Natta as early as 1954, but proof of their existence in solutions and in melts has not yet been obtained. The detailed studies of Pino have been of considerable assistance in the elucidation of the nature of the secondary structures of poly-α-alkenes. Evidence in support of the suggestion that spiral structures are present is provided by the high degree of stereoregularity, the high melting points, and the increased values of $[\alpha]_D$, which exceed the values for the monomers and model compounds by a factor of 5–30. The magnitude of $[\alpha]$ depends to a marked extent on the stereoregularity of the polymers and tends towards a limiting value[53] with increase in stereoregularity. For stereoregular specimens, the optical rotation is less sensitive to change in the regularity of the structure[53]. The absolute value of $[\alpha]_D$ for polymer solutions decreases with temperature, and the isotactic fractions show an unusually high temperature coefficient, close to the values found for solutions of proteins and polypeptides (for example, 0.30 for silk fibroin). The magnitude of $[\alpha]_D$ depends on the structure of the side-chain of the polymer, and there is an optimal distance (n = 1) between the asymmetric centre in the side group and the main chain:

Pino regards all these facts as confirmation of the existence of secondary formations analogous to the α-spirals of proteins or polypeptides[56] in solutions of poly-α-alkenes, in melts, and in the solid state.

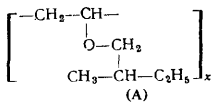
Since the contribution of the spiral structures to the total rotation increases the total rotation, decrease in $[\alpha]$ may serve as an indication of a decrease in the stereoregularity of the main chain of the polymer structure; this is also indicated by a marked negative temperature coefficient $\Delta[\alpha]/\Delta t$, characterising the reversible disappearance of regular spiral segments in the macromolecular chain with increase in temperature.

Calculation by Brewster's semiempirical method[57] established that monomers with the (*R*)-configuration form isotactic polymers in which right-hand spirals predominate.

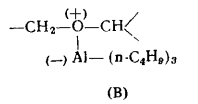
Despite the fruitfulness of this interpretation of the characteristic features of the structure of poly-α-alkenes, however, increasing doubt has recently been cast on the correctness of this interpretation[58] and it has been suggested that hindered conformations, and not spirals, are present.

Experimental data obtained by Pino and coworkers on optically active poly-α-alkenes and vinyl ethers in the presence of dissymmetric catalysts are given below.

The existence of rigid conformations, possibly of a spiral type, was suggested by Pino and coworkers[46] for the polymerisation of (*S*)-2-methylbutyl vinyl ether ($[\alpha]_D^{20}$ = +6.68°). In toluene solution, the polymer had a low rotation ($[M]_D^{25}$ = +1.1°), which was independent of the stereoregularity (infrared spectra and X-ray diffraction data) of the polyether and changed little with temperature ($\Delta[M]/\Delta t$ = +0.02). This behaviour was attributed to the presence of the ether oxygen between the asymmetric group and the main chain, weakening the steric interaction (A):



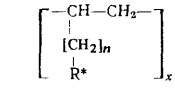
(A)



(B)

As a result, according to Pino[47], formation of a secondary structure takes place in the chain. If, however, the effect of the ether oxygen is eliminated by binding the group in a complex with $Al(n\text{-}C_4H_9)_3$, the polymer shows a sharp increase in $[M]_D$, and the temperature coefficient acquires a negative sign and a high value (up to −0.37), close to the values found for poly-α-alkenes (for example, 0.28 for poly-[*S*]-5-methylheptene). Moreover, a clearly defined dependence of $[M]_D$ on the stereoregularity of the structure is observed. All this suggested that in the "complexed" polymer one of the spiral structures predominates, as a result of the restriction of the free rotation about the C–O–C bonds in the complex (B).

A large amount of experimental material[40,59] has accumulated on the catalytic synthesis of optically active polyalkenes of general formula:



Usually, optically active monomers were employed as starting materials, and complex catalysts $Al(n\text{-}C_4H_9)_3$–$TiCl_3$ were used. The polymers were fractionated and the relationship between the optical rotation and stereoregularity was studied.

Table 4. Optical rotation of solutions of poly-α-alkenes.

	$[\alpha]_D$ monomer	Polymers					
		α_D, deg	$[\alpha]_D$, deg	$[M]_D^{20}$, deg	$\frac{\Delta[\alpha]}{\Delta t}$	$\frac{\Delta[M]}{\Delta t}$	$[\eta]$
Poly-(*S*)-3-methylpentene	(*S*) + 34.2		35.5	104	−0.10	−0.23	0.08
				163		−0.36	0.8
(*S*)-2,3-Dimethylpentane			−14.4	−11.4			
Poly-(*S*)-4-methylhexene	(*S*) − 2.5		28.6	+153	0.66	−0.42	1.3
				+288		−0.68	5.15
				+21.3			
				+9.9			
Poly-(*S*)-5-methylheptene	(*S*) + 9.8	0.95	56.5	58.1	−0.25	−0.34	5.80
Ditto, melt		0.96	—		−0.30		
Ditto, cryst.		1.02	59.6		−0.01		
(*S*)-2,5-Dimethylheptane				11.7			
(*S*)-3-Methylheptane				11.4			
Poly-(*S*)-6-methyloctene				+20.4	—	−0.09	3.78

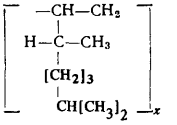
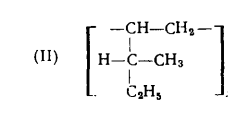
Table 4 gives data on the optical rotation of the poly-α-alkenes obtained, the monomers, and the corresponding model compounds. Sometimes, for example, for poly-(*S*)-3-methylpentene, $[\alpha]$ for the model with low molecular weight and the same absolute configuration of the asymmetric atom in the side-chain is not only smaller in magnitude, but even of opposite sign. On polymerisation, the sign of the rotation of the polymers coincides with that of the monomer, and inversion of the configuration does not take place. Inversion of the configuration is observed only for poly-(*S*)-4-methylhexene, just when there is optimal asymmetrisation of the polymer chain ($[M]_D$ = +286°).

Comparison of $[M]_D$ for model compounds (the corresponding alkanes) given in Table 4 with $[M]_D$ for the atactic fractions of poly-α-alkenes with low molecular weight shows that their rotations are of the same order of magnitude, whereas for the isotactic fractions $[M]_D$ is greater by one order of magnitude; the temperature coefficient of molecular rotation of the latter is also much greater (0.2–0.7) than that for fractions with lower stereoregularity.

The firm of Montecatini has obtained patents[48-50] on the preparation of optically active poly-α-alkenes from the corresponding monomeric (*S*)-(+)-3-methylpentene, (*S*)-(−)-4-methylhexene, (+)-3-phenylpentene, and (+)-5-methylheptene, or their antipodes, under the influence of a $TiCl_4$–$Al(n\text{-}C_4H_9)_3$ catalyst.

Pino and coworkers[44] suggest that the high optical rotation of poly-α-alkenes results from the algebraic summation of the relatively weak influences of the asymmetric atoms in the side groups and the much greater influence of the spiral structure of sections of the main chain which have identical rotation and are present in solutions.

This view appears to be confirmed by the marked dependence of the rotation on the stereoregularity of the polymers. The presence of atactic sections of chain in the polymer should decrease considerably the proportion of spirals of one sign, and hence $[\alpha]_D$. In this instance, the structure of the side group acquires considerable importance. Even when the asymmetric carbon atom is in the α-position relative to the main chain, as, for example, for poly-*R*-(−)-3,7-dimethyloctene (I), a decrease in $[M]_D$ is observed relative to the value of $[M]$ for poly-3-methylpentene (II):[51]

(I)  (II) 

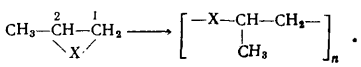
Fractionation of the poly-3,7-dimethyloctene fraction with $[\eta] = 6.52$ and $[M] = 144°$ at various temperatures (34–80°C) increased the rotation only to $[M]_D = 154°$ ($[\eta] = 6.93$).

Comparison of the properties of two groups of poly-α-alkenes, obtained by two methods: (a) by catalytic asymmetric synthesis, and (b) from the optically active monomers, shows that in the latter there is a marked increase in optical rotation as a result of the conformational contribution from the main chain, whereas the polymers obtained by asymmetric synthesis owe their optical activity to the configuration of the asymmetric atoms in the main chain.

V. STEREOSPECIFIC CATALYSIS IN THE POLYMERISATION OF PROPENE OXIDE AND IMINES

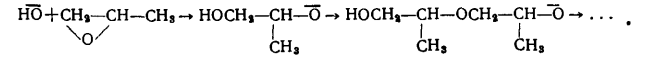
A number of problems of the detailed mechanism of polymerisation can be solved by studying the reactions of optical isomers instead of the racemates usually employed. Of particular interest are problems related to the determination of the part played by a heterogeneous catalyst in a stereoselective or stereo-elective process, the determination of the influence of the asymmetrising stages of polymerisation on the properties of the polymer produced, and the determination of the nature of the active centres of a stereospecific catalyst by comparison of the rates of polymerisation of the optical isomers and the racemate. In this connection, some success has been achieved with propene oxide—the simplest monomer capable of existing in an optically active state.

The overall polymerisation scheme assumes rupture of the epoxide ring (X = O) at the C_1–O or C_2–O bond;



If the rupture of the bonds is equally probable, as, for example, in the polymerisation of D-(+)-2,3-epoxybutane, the action of, for example, the catalytic system $Al(n\text{-}C_4H_9)_3$–H_2O in heptane gives an inactive polymer with the *meso*-diisotactic structure, with properties identical with those of the polymer from the racemic monomer[60]. Treatment of *cis*-2,3-epoxybutene with an optically active catalyst obtained from $(C_2H_5)_3Al$, acetylacetone, and *l*-menthol, however, gives a diisotactic polymer with $[\alpha]_D^{25} = +1.1° \pm 0.3°$. Inversion of the configuration of the monomer takes place in the reaction[61]. In the discussion of papers on the polymerisation of propene oxide, mention must be made of the erroneous assignment of (+)-propene oxide to the L-series[62,63]. It is more correct to relate (+)- and (−)-propene oxides to the D- and L-series respectively[64,67]. In this instance it would probably be more appropriate to use the nomenclature system of Terent'ev and coworkers[68].

The polymerisation of an optical isomer of propene oxide was first attempted by Levene and Walti[64]; the action of KOH solution gave a cyclic trimer with $[\alpha]_D^{20} = -43.0$ and a tetramer with $[\alpha]_D^{20} = -49.19$. By the action of powdered potassium hydroxide at 25°C on the D-isomer with $[\alpha] = +14.75°$, Price and Osgan[69] (1956) obtained a crystalline polymer ($\eta_{sp}/c = 0.13$; $[\alpha]_D^{25} = +25 \pm 5°$ chl., m.p. 56°C), whereas the racemic monomer gave a viscous polymer whose molecular weight, however, was similar (3000–5000), indicating a chain reaction mechanism



The use of the Pruitt–Baggett catalyst[70] ($FeCl_3$ + propene oxide) on (−)-propene oxide also gives a crystalline polymer (m.p. 72°C) with the same value of $[\alpha]_D$ as that obtained using KOH, but in addition, an amorphous fraction is always produced (from both the *l*-isomer and the racemate). Water acts as a co-catalyst, and the proportion of crystalline fraction increases in its presence. This interesting observation was subsequently applied to produce new asymmetric catalytic systems[66]. According to Price, the formation of a completely crystalline polymer from the *l*-monomer on KOH and the formation of a partly crystalline polymer on the $FeCl_3$ catalyst indicates preservation of the configuration in the first instance and partial racemisation in the second instance.

For catalysis on the $FeCl_3$ catalytic system, it was found that the rate of polymerisation is independent of the monomer concentration, but proportional to that of the catalyst, and that the degree of depolymerisation is inversely proportional to the catalyst concentration and increases with increase in the degree of conversion. This indicates that the polymerisation is heterogeneous[69], that the crystalline polymer is formed on the catalyst surface, and that the amorphous fraction is formed in solution in the presence of dissolved catalyst. This scheme presupposes asymmetric adsorption of the substrate, and this was later proved.

According to Price, the reaction mechanism involves "coordinative growth of the chain" as a result of coordination in the transition state to give a five-membered ring. The influence of water on the crystallinity of the polymer is due to its reaction with the catalyst and the creation of considerable steric hindrance in the reaction. The attachment of the first molecule of monomer takes place with preservation of the configuration of the asymmetric atom. The next molecule forms a coordinate bond with the iron atom, and this bond is formed preferentially by molecules with the same configuration. (The various reaction schemes are examined by Gaylord and Mark[71].) Other views on the mechanism of this reaction are given in a review by Bakalo and Krentsel'.[72]

Ziegler–Natta catalysts can also be used for the reaction; this gives a polymer with the same melting point as Price's polymer, indicating that the racemic polymer contains monomer chains with a single configuration[71,73].

Racemic isotactic polypropene oxide can be separated, albeit only slightly, into optically active fractions by chromatography on saccharose and on the complex formed by diethylzinc with *l*-menthol or borneol[74].

On the basis of a large amount of experimental data it is assumed that stereospecific polymerisation is facilitated by the orientating influence of the surface of a heterogeneous (or microheterogeneous) catalyst, although data have recently been published on the preparation of isotactic and syndiotactic polymers under conditions of homogeneous polymerisation by the methods of not only ionic polymerisation but also radical polymerisation[75–77]. At the same time it is known that soluble catalytic systems are less active, and the polymers obtained show a lower degree of stereoregularity[71]. This is confirmed by the data of Price and coworkers on the polymerisation of propene oxide. The fact that these microheterogeneous systems may be visually homogeneous[72] does not prove the absence of heterogeneous formations[78]. Moreover, heterogeneity may be produced in situ[71] as a result of the reduction of metal salts in the catalytic complex. The existence of active, purely heterogeneous, catalysts for the polymerisation of propene oxide also confirms this view.

Krylov and Livshits[11–13] showed that it is possible to use magnesium oxide, oxalate, and tartrate and a number of other heterogeneous catalysts for the polymerisation of propene oxide, and that the activities of Be, Ca, and Mg oxalates are comparable with that of the most effective of Price's catalysts.

A number of important problems of stereospecific catalysis have been studied for the example of the heterogeneous polymerisation of the optical isomers of propene oxide. In polymerisation on a heterogeneous catalyst, three examples of stereochemical correlation are possible: (1) the active centres of the catalyst are stereochemically indistinguishable for adsorption of the (+)- and (−)-isomers of the monomer; the probability of growth and the rate of polymerisation of the (+)-monomer are then double those for the racemate; (2) the catalyst contains equal quantities of enantiomorphic centres; the rates of polymerisation of the isomer and racemate will be equal, since replacement of the racemate by the (+)-isomer decreases the number of available centres by a factor of two but increases by a factor of two the probability of growth of the *ddd*-chains; (3) the catalyst contains centres with the same sign; the rate for one isomer will be greater than the rates of polymerisation of the other isomer and the racemate. Livshits, Krylov, and Klabunovskii[2,79,80] studied the kinetics of the polymerisation of (+)-, (−)-, and (±)-propene oxide on the heterogeneous catalyst magnesium oxalate and found that the probability of chain growth from the optical isomer [(+)- or (−)-propene oxide] is twice that for the racemate (the ratio of the first-order rate constants was ~ 2).

The results obtained (Table 5) indicate that the first situation is realised, that is, the active centres on the catalyst are indistinguishable with respect to the (+)- or (−)-isomers, and the number of accessible centres is the same for the antipode and the racemate.

In this section we must also consider the polymerisation of imines—the nitrogen analogues of propene oxide. Propeneimine isomers with $[\alpha]_D = -12.8°$ and $+12.4°$ have been polymerised in the presence of a number of catalysts [including $BF_3.(C_2H_5)_2O$] with the formation of solid polymers with $[\alpha]_D = +190.27°$ or $-101.46°$ and m.p. = 83° or 73°C respectively. Inversion of the sign of rotation takes place on polymerisation, as with propene oxide. The racemate under the same conditions gave a polymer with m.p. 17°C, although their molecular weights were similar[81].

The polymerisation of oxides and imines probably involves a succession of S_N2 reactions, in which first hydroxide ions and then alkoxide ions function as nucleophilic reagents[82]:

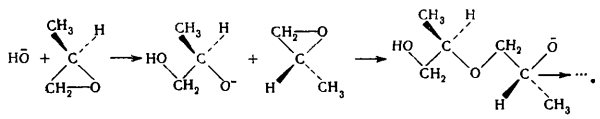
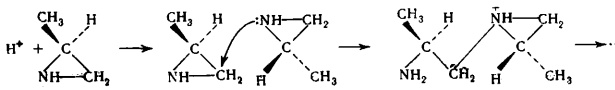


Table 5. The polymerisation of D-(+)- and L-(−)-propene oxide on magnesium oxalate and the properties of the polymers obtained.

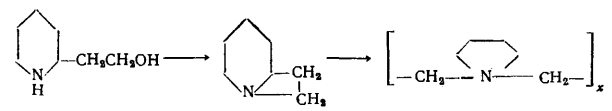
$[\alpha]_D^{20}$ for monomer, deg	Temp. of experiment, °C	Weight of MgC_2O_4, g	Duration of reaction, h	Degree of conversion, %	Polymer		Ratio of rate constants
					$[\alpha]_D$ (benz.), deg	$[\eta]$	
+9.50	83.9	0.15	33.5	74.2	−24.2	0.12	—
9.50	89.4	0.208	11.5	59.8	−23.1	0.12	1.9
9.50	93.4	0.207	14.0	54.5	−31.9	0.06	2.2
−6.95	89.4	0.242	13.5	41.1	+12.8	0.18	2.1

In the polymerisation of propeneimine we must also assume an S_N2 mechanism initiated by a proton:



Similarly, isobutylethyleneimine with $[\alpha] = -24.6°$ ($-15.4°$ [83]) gave a polymer with m.p. 56°C and $[\alpha]_D^{20} = +66.7°$ or 68° (benz.).[84] The polymer was used successfully as catalyst in an asymmetric cyanohydrin synthesis[84].

Polyconidine, prepared by Toy and Price[85], is of equal interest in connection with the use of polymers as models of enzymatic asymmetric systems. If the polymerisation is carried out in the presence of BF_3, the catalyst enters the polymer chain; the resulting polyconidine has $[\alpha]_D = +12.7°$. The action of the ether addition compound of BF_3 at room temperature gives a crystalline polymer, whose sign of rotation is the opposite of that of the monomer:



$[\alpha]_D + 11°$ $[\alpha]_D + 71°$ $[\alpha]_D - 140.8°$ m.p. 94°C

(+)-Polyconidine was obtained analogously. The racemic polymer obtained by dissolving equal quantities of (+)- and (−)-polyconidine had the same melting point as the optical isomers.

VI. THE STEREO-ELECTIVE POLYMERISATION OF DL-PROPENE OXIDE UNDER THE INFLUENCE OF DISSYMMETRIC CATALYSTS

Price and Osgan[69] found that prolonged contact between racemic propene oxide and a Pruitt–Baggett catalyst prepared using (−)-propene oxide gives a polymer containing

a crystalline fraction. This showed that under certain conditions the action of this dissymmetric catalyst may lead to a stereo-elective process, that is, the selective extraction of one of the optical antipodes of the racemate in the polymerisation. This was verified in work by Chu and Price[86]. Various catalytic systems for the polymerisation of (+)-propene oxide were studied: $Al(OC_3H_7)_3$, $ZnCl_2$, $Zn(C_2H_5)_2.H_2O$, and $FeCl_3.C_3H_6O$. All the catalysts gave crystalline polymers with similar rotations, with $[\alpha]_D$ about $-25°$, but the melting point for $Zn(C_2H_5)_2$ was much lower than that for the other catalysts, indicating a polymer with low tacticity. The polymer from the DL-monomer was even less stereoregular, however. An attempt to carry out a stereo-elective process in this way was unsuccessful.

The preparation of the catalysts involved production of the complex by the reaction of a small quantity of D-propene oxide with $FeCl_3$, after which the main bulk of the DL-monomer was added. Optically inactive products were also obtained using other dissymmetric catalytic systems: (−)-propene oxide + $Zn(C_2H_5)_2$ + H_2O; (−)-aluminium–propene glycol complex + $ZnCl_2$; and $(n\text{-}C_4H_9)_3Al$ + (−)-1-methoxypropan-2-ol.

The systems studied give less soluble and hence more stereoregular polymers from L-propene oxide than from the DL-monomer. Asymmetrisation of the catalyst by the introduction of a "seed" of the L-polymer did not give the catalyst stereo-elective properties.

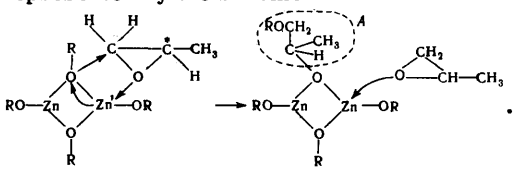
The optical activity in polypropene oxide obtained on an optically active Pruitt–Baggett catalyst was preserved only in the first hours of polymerisation at 80°C and, as shown by calculation, could be attributed entirely to the inclusion of active propene oxide from the catalyst.

The effective stereo-elective polymerisation of DL-propene oxide was carried out using a catalyst based on $Zn(C_2H_5)_2$. Polymerisation with this catalyst takes place effectively in the presence of water or alcohols. Dimeric or trimeric zinc alkoxides, whose presence was proved spectroscopically[87], are formed:

$$Zn(C_2H_5)_2 + ROH \rightarrow ROZnC_2H_5 \xrightarrow{ROH} RO{-}Zn{-}OR\,.$$

When an optically active alcohol is introduced into the system instead of water, we should expect this dissymmetric catalyst to have a stereospecific action and lead to the formation of an optically active polymer.

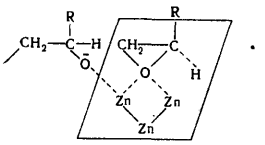
The catalytic properties of the complex are due to the presence of free coordination centres, and the zinc atom is of primary importance. For the dimer, the reaction can be represented by the scheme:



Since in the experiments the radical R was the optically active (+)-bornyl group, the introduction of each monomer molecule into the reaction sphere is sterically controlled not only by the preceding unit introduced into the chain (denoted *A* in the scheme) but also by the influence of the asymmetric centres of the bornyl group of the catalyst.

Furukawa[88] considers the polymerisation of oxides in terms of a multi-centre coordination mechanism, according to which there are two coordination centres, and the propene oxide molecule is joined through oxygen to two zinc atoms. One of the bonds is an ordinary ionic bond and involves the counter-ion.

In this coordination-anionic polymerisation, the attachment takes place at the α-carbon atom of the monomer, which contains the key atom. The stereoregulating action is brought about by the reaction of the R group in the monomer with the ligand of the catalyst or with the R group in the polymer chain. The monomer, coordinating to two catalyst centres, preserves a definite position in space relative to the end of the polymer chain and to the catalyst. The attachment of the next monomer takes place in the same configuration, with the formation of an isotactic structure. The appropriateness of this approach followed from papers by Price (1959) and the experiments of Furukawa (1962),[89] and was confirmed in work by Tsuruta and coworkers[90,91]. Asymmetric induction takes place by the stereoregular control of the reaction of the OR alkoxy-group of the optically active alcohol joined to the complex catalyst (Inoue, Tsuruta, and Furukawa[92]):



The dissymmetric catalyst was obtained, for example, by adding 0.05 M HOR[(+)-borneol, (−)-menthol] to 0.025 M $Zn(C_2H_5)_2$. At 80°C the degree of conversion in the polymerisation of DL-propene oxide amounts to 17–30%.

The crystalline polymer obtained exhibited optical activity. The conditions of the stereo-elective polymerisation, and the constants of the polymer, are given in Table 6.

Table 6. Stereo-elective polymerisation of DL-propene oxide on $Zn(C_2H_5)_2$ + co-catalyst.

Co-catalyst	Medium	% conversion	Crystalline polymer					Amorphous polymer	
				in benzene		in chloroform			
			η/c	α obs., deg	$[\alpha]_D$, deg	α obs.,, deg	$[\alpha]_D$, deg	η_{sp}/c	α obs., deg
(+)-borneol	toluene	27.6	5.63	−0.07	−5.9	+0.26	+7.4	—	—
ditto	hexane	25.0	3.30	−0.06	−4.6	+0.19	+6.1	1.48	±0.01
ditto	benzene	30.0	3.65	−0.06	−3.7	+0.04	+2.5	1.70	±0.01
(−)-menthol	ditto	17.3	0.59	−0.02	−3.6	+0.07	+2.2	—	—

A noteworthy feature is the very low values of the rotation, which lie, for example when the (−)-menthol co-catalyst is used, at the limits of error of the measurement (−0.02°). In chloroform, however, the magnitude of the rotation increases and its sign changes, confirming the presence of an optically active polymer. The amorphous fraction of the polymer did not exhibit optical activity. The molecular weights of the polymers were sufficiently large to exclude the influence of terminal groups on the total rotation, and the sign of the rotation was opposite to that of the bornyl or menthyl ether, confirming that the fragments of the optically active alcohol had almost no influence on the rotation of the polymer, although the introduction of terminal groups from the catalyst into the polymer was subsequently proved. It was also confirmed using the catalyst 9,10-di(hydroxymethyl)anthracene–dibutylzinc. The polymer obtained contained alkoxy-groups, which were identified from their ultraviolet fluorescence.

The observed inversion of the optical rotation of poly(propene oxide) from negative in benzene to positive in

chloroform is a characteristic feature, which was also observed by Price for the (−)-polymer. The curves for the dispersion of the rotation, recorded in these solvents, are completely symmetrical. It may be assumed that this sensitivity of the optical rotation to the nature of the solvent is due to the contribution of the molecular asymmetric structures of the polymer to the total rotation[92].

The magnitude and sign of the rotation are influenced considerably not only by the solvent but also by the concentration of the polymer in chloroform. This is possibly due to the formation of hydrogen bonds between the oxygen atom in the polymer and the chloroform[13]. The point of inversion lies at about 2.2 g in 100 g solution; the negative rotation increases with increase in the concentration of polymer in chloroform.

As expected, the unreacted propene oxide isolated after polymerisation acquires optical activity. Thus when the diethylzinc–(+)-borneol system was used, the monomer remaining had $[\alpha]_D^{20} = -0.98° \pm 0.05°$ so that the (+)-isomer in the racemate reacted more rapidly, enriching the monomer in the (−)-isomer[93].

If k_i and k_p are the rate constants for the initiation and propagation of the chain, it follows that if the catalyst centres are equivalent $k_{il} = k_{id}$, a mixture of *d*- and *l*-polymer chains in equal proportions is formed. On a dissymmetric catalyst, containing, for example, (+)-borneol, $k_{id} > k_{il}$ and the polymer contains more D-units than L-units. Thus more of the D-(+)-isomer is withdrawn from the racemate during polymerisation.

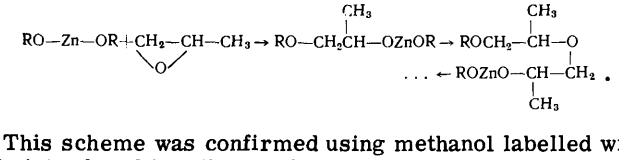
Analysis of the material balance from the optical rotation of the polymer and the activated monomer indicated that in the amorphous fraction of the polymer the influence exerted on the rotation by the bornyl group entering the polymer as terminal group cannot be neglected, since the molecular weight of this fraction is low. For the crystalline polymer, on the other hand, this influence can be neglected, in view of the high molecular weight.

The calculation is based on the formula[62,94]:

$$A\alpha_M = KP_x[\alpha_x],$$

$$K = \frac{[\alpha_{ML}]}{[\alpha_{pL}]} \cdot \left(1 + \frac{P_S[\alpha_S] + P_A[\alpha_A]}{P_x[\alpha_x]}\right),$$

where $[\alpha_{ML}]$ and $[\alpha_{pL}]$ are the specific rotations of the pure L-monomer and the polymer, A the ratio of the returned monomer to the original monomer, P_x, P_S, P_A and $[\alpha_x]$, $[\alpha_S]$, $[\alpha_A]$ the yields in per cent and the specific rotations of the crystalline, semi-crystalline, and amorphous fractions of the polymer; and $[\alpha_M]$ the specific rotation of the returned monomer. Calculation on the basis of the experimental data[62,94] showed that the plot of $P_x[\alpha_x]$ against $M[\alpha_M]$ is a straight line, indicating that K in the equation is constant, and hence that the optical activity of the polymer appears as a result of the polymerisation of the (+)-isomer in the racemate. The fact that the (+)-bornyl group can enter the fraction with low molecular weight in the polymerisation process follows from the mechanism of the initiation:



This scheme was confirmed using methanol labelled with ^{14}C, introduced into the catalytic system.

The radioactivity was found chiefly in the fraction with low molecular weight ($\bar{M}_n$ = 6100) and to a slight extent in the fraction with high molecular weight ($\bar{M}_n$ = 50000). Thus the alcohol radical enters chiefly the amorphous fraction of the polymer. Its optical activity is due to the introduction of the bornyl group, whose rotation in chloroform is positive, like that of bornyl alkyl ethers.

Experimental data[90] obtained with the $Zn(C_2H_5)_2$–(+)-borneol catalytic system show that the optical activity of the monomer increases with time as far as 70 h, and then decreases, like the proportion of crystalline fraction. The optical activity of the polymer, however, increases slightly with duration of polymerisation, and the value of $[\eta]$ does not show a definite pattern, although it changes in the same sense as the change in the specific rotation of the polymer.

Livshits and Krylov[11–13], following Price, tried to initiate the stereo-elective polymerisation of DL-propene oxide by modifying magnesium oxalate with the (−)-isomer of propene oxide or the (−)-polymer.

The influence of added polymer on the rate of polymerisation was examined above; this is also observed in the polymerisation of benzofuran[32,95], but the effect can evidently also be expected when stereoregular structures with sufficiently high molecular weight are formed in polymerisation. In this instance there is in fact an intensification of the stereospecificity of the action of the catalytic system when the optically active polymer is introduced during polymerisation.

In the example studied[11–13], the addition of polymer to the catalyst did not lead to asymmetric polymerisation, but it nevertheless facilitated the formation of a crystalline stereoregular structure in the optically inactive polymer.

Magnesium oxide and iron oxide modified with D-tartaric acid polymerised DL-propene oxide in 18% yield with the formation of a crystalline fraction of polymer with low optical activity: $[\alpha]_D^{20} = 1.4° \pm 0.3°$ and $[\eta] = 0.57$. Magnesium oxalate was modified with D- and L-propene oxide and used in the polymerisation of the racemic epichlorohydrin. This did not lead to a stereo-elective process; the polymerisation of each monomer was kinetically independent. Only magnesium tartrate proved to be an effective catalyst (Table 7).

Table 7. Stereo-elective polymerisation of DL-propene oxide on magnesium tartrate[11–13].

Magnesium tartrate, g	*dl*-Propene oxide, g	Degree of conversion, %	Polymer	
			$[\alpha]_D$, deg	$[\eta]$
0.223	4.352	10.3	−9.2	0.03
0.153	4.472	4.32	−15.6	0.24
0.690	8.368	1.67	−27.4	0.11
0.816	6.764	2.08	16.1	0.53

In the first stages of the reaction, the polymer obtained is optically pure, but its optical purity subsequently decreases. An analogous phenomenon was also observed in the polymerisation of benzofuran[96], and this can be attributed to the stage of asymmetric initiation, and not asymmetric growth. Attempts to carry out the stereo-elective polymerisation of DL-propene oxide on iron tartrate and magnesium glutamate were unsuccessful. Magnesium tartrate proved to be an effective dissymmetric catalyst, capable of bringing about not only the polymerisation of optical isomers, but also the stereo-elective polymerisation

of racemate with the formation of polymers with a high degree of optical purity (Table 7). (The specimen obtained by Price[86], with $[\alpha]_D = -28.6°$, was taken as the optically pure polymer.) In the series of catalysts magnesium oxide–magnesium oxalate–magnesium tartrate, the specific catalytic activity decreases (30 : 20 : 1), due to the increasing degree of screening of the magnesium ion, which is regarded as the active centre[11], by the organic anion. A coordination reaction mechanism, involving chemisorption of the monomer molecule and the formation of a bond between the oxygen of the ring and the coordinatively unsaturated metal ion on the catalyst surface, is assumed. Because of steric hindrance, coordination and growth are possible only when anion vacancies are present. In the oxalate these vacancies are symmetric, whereas in the D-tartrate the vacancies are dissymmetric, and this is responsible for the stereo-elective character of the polymerisation of propene oxide. The importance of anion vacancies is also emphasised in the examination of the mechanism of action of Ziegler–Natta catalysts[9,97]. This view differs essentially from earlier views[98], according to which the stereospecificity of heterogeneous polymerisation catalysts is associated with a regular crystal lattice, and lattice defects can have only a negative influence on the stereospecificity of the catalyst.

Japanese workers were able to obtain reproducible results in the stereo-elective polymerisation of DL-propene oxide on a diethylzinc–borneol catalytic system, and this enabled them to undertake a detailed study of the mechanism of stereospecific catalysis and an investigation of the part played by asymmetric adsorption.

Tsuruta and coworkers[63] studied the "copolymerisation" of the D- and L-isomers using a stereo-elective catalytic system and, for comparison, using the non-specific catalyst KOH. Neither KOH nor $Zn(C_2H_5)_2$–CH_3OH exhibit stereoselectivity, and in the polymerisation of (+)-propene oxide the original monomer and the returned monomer have the same specific rotation. The plot of $[\alpha]_D$ for the non-fractionated polymer against $[\alpha]_D$ for the original monomer is a straight line for both catalysts, and if racemisation takes place in the reaction, it does so to an equal extent on KOH and $Zn(C_2H_5)_2$–CH_3OH.

When $FeCl_3.C_3H_6O$ was used as catalyst, the monomer with $[\alpha]_D = +15°$ gives a polymer with $[\alpha]_D^{20} = +17°$ (chloroform), that is, with a higher degree of racemisation than that in the example studied[63]. If the polymer is fractionated, the more crystalline fraction has a higher specific rotation than the amorphous fraction, so that the quantity of D-isomer entering the crystalline polymer is greater than that corresponding to the D/L ratio in the original monomer.

This is due to the fact that for a ratio D/L > 1 in the monomer, the rate of formation of a bond between the D-molecule and the active centre D* will be greater than the rate of formation of a bond between the L-molecule and this centre, so that $k_{DD}* > k_{LD}*$, despite the fact that the numbers of D*- and L*-centres on the non-specific catalyst [KOH or $Zn(C_2H_5)_2$–CH_3OH] are equal[63]. As a result, the ratio D/L in the polymer is greater than that in the monomer. Thus on a non-stereospecific catalyst $k_{DD}*k_{LD}* = k_{LL}*k_{DL}*$, whereas on a specific catalyst this equality is not observed, and the distribution of the D*- and L*-centres will be unsymmetrical.

Not only alcohols, but also ethers and amines[99], can be used as optically active modifying co-catalysts for carrying out "asymmetrically selective polymerisation".[66]

Stereo-elective power is also shown by a catalyst consisting of the reaction mixture of the partial hydrolysis of the $FeCl_3$–C_3H_6O catalyst, carried out in the presence of *d*-bornyl ethyl ether (*d*-BEE). This system was found to be highly effective and led to optical activation of the unreacted propene oxide with the formation of a crystalline polymer which, to the surprise of the authors, was found to be optically inactive. This phenomenon is so interesting that it is worth considering in more detail.

The catalyst was prepared by the Pruitt–Baggett and Price methods[69], after which *d*-BEE and water were added. The optimum Fe : H_2O : BEE ratio was found to be 1 : 1.5 : 0.5 (the returned monomer in this instance had $[\alpha]^{13} = +1.94°$, but the crystalline and amorphous fractions of the polymer were optically inactive). The rotation of the monomer increased with time, from +0.22° (1.4% activation) to 1.19° (7.9% activation).

Thus the (−)-isomer polymerises more rapidly, but the numbers of units with the *d*- and *l*-configurations in the polymer are equal and the polymer does not show optical activity.

The discovery by Furukawa and coworkers[66] of asymmetric adsorption on the catalytic system studied is of extreme importance. When DL-propene oxide was added to the system at −20°C, the excess distilled off in a vacuum, and the adsorbed quantity displaced by the addition of triethylamine, the propene oxide fractions obtained had optical rotations with different sign: $[\alpha]'_D = +0.084°$ and $[\alpha]''_D = -0.42°$.

It can thus be seen that the concentration of (−)-isomer on the surface of the complex is greater than that of the (+)-isomer, and the sign of rotation corresponds to the antipode which is polymerised at a greater rate by the given catalytic system. Thus asymmetric adsorption is one of the chief factors determining the reactions of *d*- and *l*-isomers. Kinetic treatment of the results showed that the ratio of the rates of polymerisation is close to the ratio of the isomers adsorbed on the catalyst.

The reaction takes place by a coordination-anionic mechanism, in which the monomer is first coordinated to the active centre (activated by adsorption), after which opening of the epoxide ring takes place. This can be represented by the scheme:

$$D \overset{K_D}{\rightleftarrows} D_{ad} \xrightarrow{k_D} \text{polymer}$$

$$L \overset{K_L}{\rightleftarrows} L_{ad} \xrightarrow{k_L} \text{polymer}$$

where K_D and K_L are the constants for the adsorption equilibrium, and k_D and k_L the rate constants for opening of the ring.

The rate of polymerisation is proportional to the concentration of adsorbed monomer, that is

$$\frac{dD}{dL} = \frac{k_D[D_{ad}]}{k_L[L_{ad}]} = \frac{k_D K_D[D]}{k_L K_L[L]},$$

or

$$\ln\frac{D}{D_0} = \frac{k_D K_D}{k_L K_L}\ln\frac{L}{L_0} = r\ln\frac{L}{L_0},$$

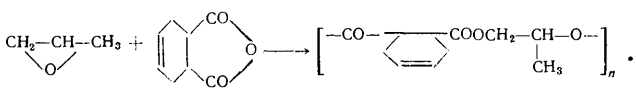
$$r_0 = \frac{k_D K_D}{k_L K_L},$$

where D_0 and L_0 are the initial concentrations of the isomers of the monomer, and r the selectivity index of the process. The inequality of the rates of polymerisation of the *d*- and *l*-isomers is controlled chiefly at the coordination (adsorption) stage. The selectivity index of the process depends essentially on the composition of the catalyst. The optimum Fe : H_2O : *d*-BEE ratio is 1 : 1.5 : 0.5, at which $r = 1.71$. The selectivity of the catalyst r increases with

increase in the water concentration and decreases with increase in the concentration of $FeCl_3$ and *d*-BEE. A second interesting observation made by Furukawa and coworkers[66] was the absence of optical activity in the polymer. Since there can be two forms of adsorption: (1) selective adsorption, when there are unequal quantities of D- and L-centres on the catalyst surface, and (2) non-selective adsorption, when the entire surface of the catalyst is equally accessible to the D- and L-molecules of the adsorbate, four states are possible, depending on whether the quantities of adsorbed D- and L-molecules are equal or unequal (non-equilibrium). Moreover, at the stage of ring opening there are four possibilities: (1) preservation of the configuration, (2) inversion of the configuration, (3) racemisation and stereospecific growth of the chain, and (4) racemisation and non-stereospecific growth of the chain. ("Racemisation" here denotes not conversion of an isomer of the monomer into the racemic monomer, but the formation of equal quantities of *d*- and *l*-units in the chain from the *d*- or *l*-monomers.) Path (3) gives equal quantities of the *d*- and *l*-polymers, whereas path (4) gives a stereoregular polymer consisting of equal quantities of *d*- and *l*-units.

In the diethylzinc–(+)-borneol and diethylzinc–water–(+)-BEE systems, processes of selective non-equilibrium coordination take place with preservation of the configuration (the formation of optically active monomer and polymer with regular structure) and racemisation with non-stereospecific growth of the chain (the formation of optically active monomer and inactive and non-regular polymer).[109]

Since propene oxide readily undergoes asymmetric selective polymerisation, it may be expected that asymmetric copolymerisation of propene oxide with another monomer having an asymmetric carbon atom will take place successfully[101]. Thus DL-propene oxide and 3-phenyl-Δ^4-tetrahydrophthalic anhydride copolymerise under the influence of 2% diethylzinc–(+)-borneol catalyst in toluene at 80°C. The copolymer (yield 49.9%) had $[\alpha]_D^{25} = +2.9°$ for a duration of reaction equal to 108 h. The rotation of the polymer, and its viscosity, increase with duration of the reaction.



The unreacted propene oxide and the propene glycol obtained by hydrolysis of the polymer were optically inactive, whereas the unchanged anhydride (isolated as the monomethyl ester) had a rotation between +1.4° and +1.7°. The dicarboxylic acid obtained by hydrolysis of the polymer was also optically active (between −0.4° and −0.5°). This unexpected result is most readily explained by assuming that the asymmetric centres of the catalyst directly activate the anhydride, which displaces the propene oxide from the D- and L-centres by adsorption.

Tsuruta and coworkers[102–105] extended stereo-elective polymerisation to the synthesis of optically active polyalanine from *N*-carboxy-DL-alanine anhydride (I), which polymerises under the influence of compounds containing active hydrogen, to form a water-soluble polypeptide. Organometallic compounds were recently used for the polymerisation of L-(I) to give a high polymer[106]. It was found that the use of even one component of the catalytic systems studied, for example, (+)-borneol or (−)-menthol as catalyst made it possible to obtain, from DL-(I), a macromolecular optically active polyalanine, which was (+) in dichloroacetic acid (DCAA) and (−) in a chloroform–DCAA mixture; the water-insoluble fraction had a high rotation (+1.3° and −1.0°).

The use of the triethylaluminium–(+)-borneol (in the ratio 1 : 2) system gave the same results: a water-insoluble fraction with $[\alpha]_D = +1.2°$ (DCAA) and $[\alpha]_D = -0.4°$ (chloroform–DCAA) was obtained in 29.5% yield.

VII. THE STEREO-ELECTIVE POLYMERISATION OF DL-α-ALKENES

Stereo-elective polymerisation has also been used successfully in the field of poly-α-alkenes. Here, two mechanisms are possible: (1) the "selection" of one of the enantiomorphs of the monomer is regulated by the asymmetric group of the chain—the alkyl group of the catalyst or the first monomeric unit, and (2) the difference in the rates for the enantiomorphs is due to the asymmetry of the active centre of the catalyst, produced as a result of appropriate arrangement of the surface atoms or by inclusion of asymmetric organic groups in the active centre.

The first possibility might be verified by comparing the optical activity of polymers from racemic 4-methylhexene and propene on an optically active catalyst. In actual fact, using a $TiCl_3$-[(+)-(*S*)-2-methylbutyl]$_3$Al.O$(C_2H_5)_2$ catalyst (optical purity 91%), Pino and coworkers[52] were able to detect optical activity in polypropene and polystyrene. Although the values found for the rotation of polypropene and polystyrene are very small, they are slightly greater than the values given by Braun and Kern[21]: +0.1 ± 0.003° for isotactic polystyrene and 0.12° for amorphous polystyrene. It should be noted that earlier, Murahashi and coworkers[20] had not detected rotation under these conditions, and Fray and Robinson[22] had not observed rotation for polypropene, either in the polymer or in the fragments obtained by pyrolysis of the polymer. Pino[52] attributed the discovery of slight activity in polypropene and polystyrene to the high optical purity of the 2-methylbutyl group in the catalyst which he used, and to the more successful selection of polymerisation conditions. In experiments at atmospheric pressure, the polypropene fractions with low molecular weight had $\alpha_D = +0.025°$ (*l*1) and $[\alpha]_D = +3.9°$, whereas the corresponding values at 10 atm were $\alpha_D = +0.05°$ (*l*1) and $[\alpha]_D = +0.90°$. For polystyrene with (*R*)-2-methylbutyl-lithium/tris(acetylacetonato)chromium catalyst the values $\alpha_D = +0.105°$ (*l*2) and $[\alpha]_D = +0.6°$ were obtained for the fraction with low molecular weight.

The stereo-elective polymerisation of racemic 4-methylhexene on a $(C_5H_{11})_3Al$–$TiCl_3$ catalyst gave an optically active polymer whose $[\alpha]_D$ value did not depend on the stereoregularity, but only on the monomer: $(C_5H_{11})_3Al$ ratio (the best result was obtained at a ratio 1 : 4) and on the molecular weight: $[\alpha] = 1.1°$ at $[\eta] = 0.15$ and falls to zero with increase in $[\eta]$ to 2.05. The highest rotation was found in the amorphous fraction, soluble in acetone: $\alpha_D = +0.095°$, $[\alpha]_D = +7.1°$.

Since one antipode entered the racemate preferentially during polymerisation, activation of the unreacted monomer due to the excess of the antipode remaining might have been expected. It was found, however, that the monomer remained inactive. Other dissymmetric catalysts were studied: [(*R*)-2-methylbutyl]Li–$TiCl_4$, [(*S*)-2-methylbutyl]$_2$Zn–$TiCl_4$, and [(*S*)-4-methylhexyl]$_3$Al–$TiCl_4$. The specific rotation of the poly-4-methylhexene fraction soluble in acetone had the values +0.7°, 13.6°, and 4.6° respectively.

Fractionation of the polymer obtained using the [(*S*)-C_5H_{11}]$_2$Zn–$TiCl_4$ catalyst gave an amorphous fraction with

$\alpha_D = +1.385°$ (*l*1) and $[\alpha]_D = +15.2°$, and a fraction with high molecular weight, with $\alpha_D = +0.030°$ and $[\alpha]_D = +1.7°$. The unreacted monomer had $\alpha_{350} = +0.045°$.

Examination of these results shows that the optical activity in polypropene and polystyrene can arise only from the introduction of terminal groups from the catalyst. At a high catalyst: monomer ratio, optical activity may appear not only in the amorphous fractions but also in the isotactic fractions. Thus the optical activity in the polymers depends not on the stereoregularity, but chiefly on the molecular weight of the fractions.

The fact that the poly-(4-methylhexene) obtained by stereo-elective polymerisation from the racemic monomer had a value of $[\alpha]_D$ comparable with the values for polypropene and polystyrene, and smaller by a factor of 10–100 than the value for poly-(*S*)-4-methylhexene obtained from the optically active monomer, and also the absence of rotation in the unreacted monomer, evidently indicate that the reaction rate is the same for both antipodes and that the catalyst groups are introduced as alkyl terminal groups into the polymer chain. Moreover, for the experiments using $TiCl_4$–$Zn(C_5H_{11})_2$ catalyst, when the greatest rotation of the polymer was observed, it may be assumed that the terminal groups themselves also have an influence by asymmetric induction, which according to calculation by Brewster's method[57] should be considerable. Despite its low efficiency, a method for the stereo-elective polymerisation of poly-α-alkenes has been patented[48–50].

The polymerisation of racemic 3,7-dimethyloctene and 3-methylpentene on a $(C_5H_{11})_2Zn$–$TiCl_4$ catalyst is stereo-elective, and the unreacted monomer remaining shows appreciable optical activity[54]. The optical activity of the polymer fractions increases with increase in stereoregularity, in contrast with cases where the activity decreases and is due to terminal groups.

Table 8. Stereo-elective polymerisation of racemic 3-methylheptene and 3,7-dimethyloctene on a $TiCl_4$-di-(+)-2-methylbutylzinc catalyst.

Monomer	Unreacted monomer		Polymerised monomer			Optical purity of polymer, %
	α_D^{25}	$[\alpha]_D^{25}$	(*S*)	(*R*)	(*S*)/(*R*)	
3-Methylheptene	—0.07 (*l* 2)	—0.75	0.15	0.10	1.5	5.5
3,7-Dimethyloctene	—0.20	—0.28	0.20	0.16	1.25	9.97
	—0.36	—0.52	0.46	0.37	1.24	1.6

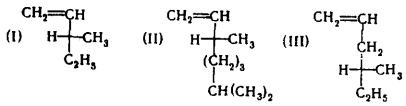
The sign of rotation of the monomer indicated that the polymerisation involves the (*S*) antipode, which has the same absolute configuration as the optically active (*S*)-2-methylbutyl group in the catalyst, whereas the excess of monomer remaining has the (*R*) configuration (see Table 8).

The (*S*)/(*R*) ratio characterises the rates of polymerisation of the antipodes in the racemate. Fractionation of poly-(3,7-dimethyloctene) gave a polymer insoluble in diisopropyl ether and soluble in cyclohexane, with $[\eta] = 0.91$ and $\alpha_D = 0.11°$ ($[\alpha]_D = +18.0$). After the fractionation of poly-(3-methylpentene), the most stereoregular fraction had $\alpha_D = 0.17°$ and $[\alpha]_D = +13.4$, whereas the fractions with low molecular weight had high rotation (+16.9°).

It was previously found that the stereo-elective polymerisation of racemic poly-(4-methylhexene) gives a polymer from which fractionation gives fractions whose optical activity decreases with increase in stereoregularity.

Stereo-elective polymerisation was achieved by Goodman and coworkers[107] using a catalyst obtained by the action of $LiAlH_4$ on *R*(−)-3,7-dimethyloctene (formation of the compound $LiAlR_4$) in its compound with $TiCl_4$. The action of this catalyst on racemic 3,7-dimethyloctene led to selective polymerisation, which depended on the value of $[\alpha]$ (between −8.3° and −11.74°) of the monomer in the catalyst, and the monomer/catalyst ratio (from 7.6 to 84.0). The specific rotation of the polymer increased from −49.6° to −83.3°.

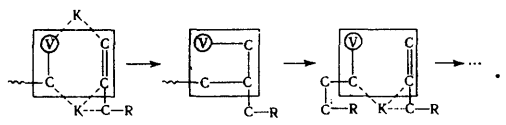
These results show that the structure of the monomer plays an important part in stereo-elective polymerisation. The catalyst is able to selectively remove one antipode from the racemate if the asymmetric atom is in the α-position to the double bond, for example, in 3-methylpentene (I) and 3,7-dimethyloctene (II); asymmetric stereo-elective polymerisation does not take place if the asymmetric atom in the side-chain is in the β-position, as in 4-methylhexene (III):



The problem of the detailed mechanism of asymmetrisation in stereo-elective polymerisation can be resolved by accumulating sufficient experimental data, but it can already be assumed that of the two mechanisms: (1) that in which the (*S*)-C_5H_{11}-group in the catalyst takes direct part in the asymmetric initiation of the polymer chain, and (2) that in which the (*S*)-C_5H_{11}-group modifies the active centre of the catalyst on which the preferential adsorption of one antipode of the monomer takes place on the transition metal, the latter is to be preferred[55], since this does not require the introduction of the concept of highly efficient 1,3-asymmetric induction with transfer along the chain of 1,3-carbon atoms. This is necessary, however, if we adopt the first scheme, which is similar to Cram's model of 1,3-asymmetric induction[108].

In actual fact, vinyl polymerisation gives 1,3-pseudo-asymmetric atoms in the chain; a polymer formed by a mechanism of 1,3-asymmetric induction will show the sequence $(ddd\ldots)_n(lll\ldots)_m$, whereas for induction due to the asymmetry of the catalytic asymmetric centre the sequence $(ddd\ldots)_n l(ddd\ldots)_m$ should predominate, that is there should be a much higher probability (p) of formation of sequences with the same configuration ($p_{dd} \gg p_{dl}$ or $p_{ll} \gg p_{ld}$), and with stereo-isomeric centres in the catalyst $p_{dd} \neq p_{ll}$.[109]

If we accept Cossee's ideas[9] regarding the part played by vacancies in polymerisation catalysis, we can picture the following mechanism, using the multiplet theory of catalysis:



Ⓥ - represents a vacancy

For α-alkenes, the adsorption of the C of the asymmetric centre outside the index is small, and the polymer is formed with preservation of the configuration[110].

Propene oxide, as a result of the strong adsorption of a carbon atom on a centre close to a vacancy, undergoes inversion of configuration (always observed for alkylpropene oxide and polypropeneimine) and the efficiency of the stereo-elective process should be slightly greater.

The concept of modification of the active centres of the catalyst by the asymmetric component is apparently more correct. This is confirmed, for example, by the stereo-elective polymerisation of racemic propene oxide when previously prepared active poly(propene oxide) is introduced on to the catalyst, as indicated above. "Autocatalysis" with benzofuran is also apparently due to some extent to this modification. The stereo-elective copolymerisation of racemic (*R*)(*S*)-3,7-dimethyloctene and (*R*)-(+)-methylpentene† can probably also be attributed to this morphological catalysis. In this connection, mention should be made of the production of asymmetrising properties in Raney nickel catalyst after modification with optically active compounds[111-113].

In conclusion, it should be noted that the high efficiency of stereoselective and stereo-elective polymerisation and the chromatographic separation of racemic polymers on other optically active polymers under conditions in which compounds with low molecular weight did not give these effects, apparently confirms Pasynskii and Pavlovskaya's view[114] that in nature, asymmetry has developed not by the formation of optically active compounds with low molecular weight, which then act as monomers, but initially by a process in which stereospecific polymerisation has led to the formation of stereoregular and then dissymmetric catalysts, on whose basis the optical asymmetry of compounds with low molecular weight began to develop, so that the origins of the latter are secondary.

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Since the present manuscript was submitted for publication, a number of new papers on asymmetric catalysis in the field of optically active polymers, including a number of particular interest[122-127], have been published[115-121].

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Macromolecular Complexes as Chemical Reaction Catalysts

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The wide potential applications of catalysis by macromolecular compounds have aroused universal interest in this relatively new branch of chemical science: the number of publications devoted to this problem has been growing continuously since the 1950's. Thus, many papers have dealt with the use of sulphonic acid resins as catalysts for hydrolysis and esterification, hydration and dehydration, alkylation, and also various condensations (see review by Polyanskii[1], recent Japanese work[2], etc.). A substantial fund of knowledge has accumulated also on the use of macromolecular catalysts and initiators in polymerisation reactions. For example, the above sulphonic acid resins have been used as polymerisation catalysts for isopentene, butene, dienes[1] and vinyl alkyl esters[3]. Macromolecular radicals obtained by chain transfer reactions[4], illumination, mechanical methods[5], or by chemical changes of reactive groups[6] are already used extensively in the synthesis of graft or block copolymers. These and other polymer systems can be synthesised also on macromolecular anions obtained as macromolecular Ziegler-Natta catalysts[7], macromolecular anion-radicals, or dianions[8], on macromolecular organometallic compounds of the polylithiumpolystyrene[9] or polylithiumpolyethylene[10] type, etc.
Papers on the catalysis of reactions by macromolecular complexes relate to the same field of research. The present review, without attempting to be fully comprehensive, deals with the most important papers (published up to 1968) on the catalysis of organic and of inorganic reactions by macromolecular complexes. For comparison, low-molecular-weight complexes are considered in a number of instances. 84 references.

CONTENTS

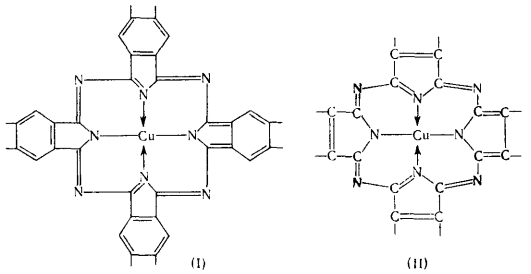
1. Redox reactions and decompositions 984
2. Polymerisation and copolymerisation 988
3. Catalytic activity and structure of macromolecular chelates 992

1. REDOX REACTIONS AND DECOMPOSITIONS

Since the earliest days of the study of catalysis by macromolecular complexes, the catalytic action of these materials towards various oxidation–reduction reactions has attracted most attention†. Among the first papers to be published in this field were those of Roginskii and coworkers[11,12], who studied the catalytic properties of macromolecular chelates with a system of conjugated bonds.

Thus, Roginskii and coworkers[11] investigated the activity of a series of poly(copper phthalocyanines) having different electrophysical properties towards the decomposition of H_2O_2. The greatest catalytic activity was found in the polyphthalocyanine which had the highest electrical conductivity at room temperature and the lowest activation energy for electrical conduction. The lowest activity was observed with the polymers of lowest electrical conductivity and highest E_{act}. The authors attempted to correlate the electrophysical properties and the catalytic activity of these polyphthalocyanines. They also attempted a correlation in their study of the oxidation of alkylaromatic and cyclic hydrocarbons on macromolecular phthalocyanines[12].

These workers compared the rates of oxidation of various hydrocarbons on copper phthalocyanines of type (I), and also the catalytic activity of polymeric and monomeric copper phthalocyanines towards the oxidation of cumene to the hydroperoxide, with the activity of polymeric complexes of tetracyanoethylene and copper, which are presumably macrocyclic azoporphyrin structures of type (II):



(I) (II)

It was found that the polyphthalocyanines are more active than their monomeric analogues and that the tetracyanoethylene polymers are more active than the polyphthalocyanines: the underlying reasons were not discussed. Manecke and coworkers[13] also examined polychelates of this type, prepared from metal acetylacetonates and tetracyanothiophen (or tetracyanofuran), *p*-phenylenedimalononitrile, or *o*-phthalodinitrile.

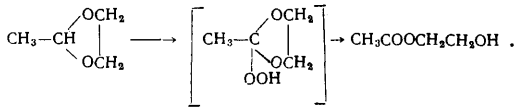
To explain the mechanism of the catalytic action of macromolecular complexes with conjugated bonds, Berlin and coworkers[14] suggest that the presence of acetylacetonate residues in the azoporphyrin structures (II) causes initiation of a chain decomposition of the polymer with formation of peroxide radicals. These workers conclude that in the oxidation of, for example, cumene, in the presence of poly(copper phthalocyanine), oxygen must be present as

† Data on the catalytic properties of low-molecular-weight complexes have long been available: for convenience in presentation we shall discuss them and compare them with the catalytic properties of macromolecular complexes of similar structure;

undissociated molecules or as radical-ions on the catalyst surface.

The catalytic activity of mixed Cu, Fe polyphthalocyanines in the heterogeneous oxidation of aldehyde acetals by oxygen was recently discussed in some interesting papers by Inoue and coworkers[15,16].

Assuming that the main product of the oxidation of acetaldehyde ethylene acetal [2-methyl-1,3-dioxolane (Ed. of Translation)] is 2-hydroxyethyl acetate (as well as acetic acid, acetaldehyde, ethylene glycol, and water), the authors propose the following reaction scheme:



The catalytic activity of this polymeric complex towards the oxidation of other acetals or of cumene is considerably lower (see Fig. 1).

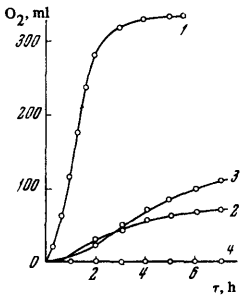


Figure 1. Rate of absorption of O_2 in the presence of Cu, Fe-polyphthalocyanine in the following oxidation reactions:
1) acetaldehyde ethylene acetal [2-methyl-1,3-dioxolane (Ed. of Translation)]; *2*) benzaldehyde ethylene acetal [2-phenyl-1,3-dioxolane (Ed. of Translation)]; *3*) cumene; *4*) acetaldehyde dimethyl and diethyl acetals.

The catalytic activity is strongly dependent on the ratio of the metals (Cu–Fe or Mo–Fe), and on the activation energy for electrical conduction of the polyphthalocyanine. It has been pointed out that these polymers are highly selective and show a synergic effect due to the interaction of two redox metal atoms through a system of conjugated bonds, since the reaction is catalysed neither by Cu-, Fe-, or Mo-polyphthalocyanines, nor by their mixtures[16].

The oxidation of hydrocarbons in the presence of low-molecular-weight chelates was known in the 1950's, and acetylacetonates as well as other chelate compounds are now used industrially for this purpose.

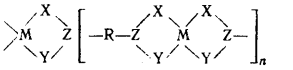
The acetylacetonates of Cu and Co are used, for example, in the liquid-phase oxidation of toluene and ethylbenzene by oxygen or air to the corresponding aldehydes and acids; the rate of the reaction is periodically increased by adding inorganic adsorbents of the Al_2O_3 or kieselguhr type[17].

Cobalt isovalerylacetonate is used industrially as a catalyst for the oxidation of primary and secondary (but not tertiary) alkylbenzenes to the corresponding acids[18]. Salcamine (bis-salicylaldiminatocobalt) is widely used in industry to deodorise petroleum (by oxidising mercaptans to disulphides with atmospheric oxygen[19]) or to remove oxygen-containing impurities dissolved in hydrocarbons[20].

Turning now to oxidation–reduction reactions on macromolecular complexes, we note that the Du Pont company[21] reported in 1962 an investigation of the catalysis of a large number of reactions in the presence of polychelates. These included the oxidation of isovaleraldehyde, metacrolein‡, furfural, and cinnamaldehyde to the corresponding acids, and the oxidation of ascorbic acid to dehydroascorbic acid; the reduction of nitrobenzene to aniline and of nitrocyclohexane to nitrosocyclohexane (cyclohexanone oxime); the reduction of metal ions (Ag, Hg, Fe) to a lower valency, etc. The structure and properties of the polychelates are not quoted: it is stated only that the macromolecular ligands used include salicyl- or resorcinol–formaldehyde resins, polythiosemicarbazides, polyoximes, polyaminostyrene-*NN*-diacetic acids, and other polyfunctional polymers.

The choice of a polymeric ligand to prepare macromolecular chelates for the catalysis of the stated oxidation–reduction reactions is mainly dictated, according to the authors, by the stability of the resulting chelate (though stability or formation constants are not quoted), whereas the metal suitable for complex formation is chosen on the grounds of its redox potential. Both these factors are known to affect the rates of reactions catalysed by low-molecular-weight complexes. Thus, Sn^{II}-polyformaldehyde salicylate reduces silver ions to metallic silver almost instantaneously, whilst Sn^{II}-polyaminostyrene-*NN*-diacetate reduces them in 10–15 min. Nitrocyclohexane is reduced quantitatively to cyclohexanone oxime in the presence of the above polychelates of Fe^{II}, Cu^{I}, and Sn^{II} in times of 24–36, 4, and 1 h respectively[21].

The reactivity of polymeric chelates of transition metals with linear or cross-linked structures (III)



(III)

and of their monomeric analogues was investigated by Boreskov and coworkers[22–25] for a number of reactions; the rates of decomposition were found to be strongly influenced both by the nature of the metal and by the structure of the organic ligand.

No correlation was found when the electrical conductivities of the polychelates were compared with their catalytic activities[22]. Thus, the Zn- and Cu-polychelates of the type 2(S, N)§ thiocarbamate have an electrical conductivity of $10^{-9}\ \Omega^{-1}\ cm^{-1}$, and the corresponding Ni-polychelates have a conductivity of the order of $10^{-13}\ \Omega^{-1}\ cm^{-1}$, and yet the catalytic activity of the Cu and Ni polychelates is high, whereas the Zn polychelates are catalytically inactive. This is probably due to the fact that chemisorption and catalysis are determined not so much by the semiconducting properties of the polymer as a whole as by the electronic state of the metal in the chelate group: the latter criterion is responsible for the strong influence of the environment of the metal in the coordination centre on the catalytic properties of the polymer.

Keier and coworkers[27–30] have shown that studies of X-ray absorption spectra are valuable in establishing the state of the metal in the coordination centres of chelate compounds. In this way, they were able to evaluate and compare the effective charges concentrated on the copper

‡ It is uncertain whether metacrolein $(C_3H_4O)_3$, or methacrolein (methacrylaldehyde, 2-methylprop-2-enal) $CH_2{=}C(CH_3)CHO$, is intended (Ed. of Translation).

§ Complexes can have a variety of coordination centres. According to Calvin and Martell's classification[26], adopted here, these can be designated 2(O,O), 2(O,N), 2(N,N), 2(S,N), 2(O,S), etc. (for bidentate ligands).

atom in the molecules of various chelate compounds, and to establish a correlation between these values and the reactivity of the polymeric chelates. They were also able to identify the direction of changes in the charge on the metal atom accompanying changes in the structure of the ligand. Thus, a direct experimental study of the interaction of polychelates of the Cu–2(S, N) type with the reactants was possible.

For example, in the decomposition of N_2H_4 the effective charge η_π^{eff} remains practically constant during the first hour, and changes by approximately $0.15e$ during the following 15 h. In the oxidation of isopropylbenzene, a change of approximately $0.2e$ (and of the opposite sign) was noted in the charge on the copper atom. Thus, the change in the charge on the central atom of the polychelate is evidence for direct interaction between the reactants and the polymer. In particular, in the decomposition of N_2H_4 partial reduction of the copper during the course of the reaction is indicated by the direction of the shift of the K absorption edge of the copper in the polychelate and by the sign of the change in the charge on the copper atom[27–30]. The X-ray K absorption spectra of copper in polychelates of the type 2(S, N) were used to evaluate η_π^{eff} as a function of molecular weight (between 600 and 3100). On increasing the degree of polymerisation, η_π^{eff} decreases non-uniformly, and on changing from the monomer to a polymer with $M = 1790$ this quantity is hardly affected (but the reactivity of the polychelate is approximately 5–6 times higher than that of the monomer). With further increase in molecular weight η_π^{eff} begins to increase, reaching $0.2e$ for a polychelate with $M = 2560$ (whose reactivity is higher than that of the monomer by a factor of 35).[29]

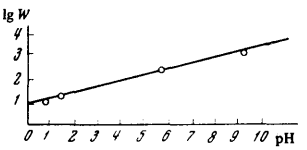


Figure 2. Variation of the rate of decomposition of H_2O_2 on the Cu polychelate of dinitrosoresorcinol with pH at 60°C (W in $cm^3\ m^{-2}\ min^{-1}$).

Because of the lack of solubility, polychelates are difficult to study by physical methods, and the authors were compelled to use much less active monomeric analogues (for example, those prepared from thiopicolineanilides).

Anufrienko and coworkers[31] showed by the ESR method that the M–X,Y bonds in compound (III) have a mainly covalent character, and Zeif and coworkers[32] determined the structure of the complexes as a whole by ultraviolet and infrared spectroscopic studies. Using an approximate quantum-mechanical method of calculation, the nature of the change in effective charge (η_π^{eff}) of the metal ions in the chelate group on varying the structure of the organic ligand was characterised from experimental ultraviolet spectra; in this way, the relationship between the rate of decomposition of hydrazine and the change in effective charge was investigated for a series of chelate complexes. We should note that the application of all these methods has revealed a substantial change in the copper chelate during the decomposition of N_2H_4, which obviously points to chemical (as distinct from catalytic) decomposition of hydrazine under the conditions used in this work[25,33].

According to the same authors[34], the catalytic activity of the polychelates is higher than that of their low-molecular-weight analogues by at least an order of magnitude. They conclude that the higher activity of the polychelates is associated with disorder and distortion in the structure of their chelate groups. Furthermore, the catalytic activity can be influenced by the presence of uncomplexed metal ions at chain ends, which is itself very sensitive to the conditions of preparation of the polymers.

Boreskov and coworkers consider[34] that their observations on the reactions catalysed by macromolecular chelates show a similarity to the characteristic features of the catalytic properties of enzymes, and that chelate polymers are a type of heterogeneous catalyst occupying an intermediate position between inorganic catalysts and enzymes. In this connection, they examined the catalytic activity of synthetic polymeric chelates towards the liquid-phase decomposition of hydrogen peroxide, one of the simplest organometallic enzyme reactions[35]. Kinetic isotherms for this reaction on polychelates of the 2(o, o) type with different metal atoms were obtained; on raising the pH the rate of the reaction increased by almost two orders, evidently as a result of the greater degree of dissociation of the hydrogen peroxide. The reaction rate varies linearly with pH over a wide range of pH values (Fig. 2). The authors believe that the rate of the heterogeneous decomposition of H_2O_2 on each surface centre of the copper polychelate is close to the value found for the enzyme catalase[35].

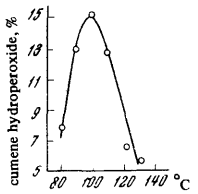


Figure 3. Concentration of cumene hydroperoxide in the oxidised material as a function of temperature of the oxidation in the presence of a 2(S,N) Cu polychelate.

Keier and coworkers[36] studied the catalytic properties of Cu- and Ni-polychelates of the 2(S, N) type based on the bis-thioamides of quinaldine towards various reactions, including the oxidation of isopropylbenzene (cumene) to the hydroperoxide by atmospheric oxygen (Fig. 3). Although in this instance the catalytic activity (which is greatest for the Cu polychelates) and selectivity are determined by the metal ion, the structure of the ligand also plays a role. By introducing electron-donor groups (CH_3, OCH_3) into the biphenyl unit of the polymer chain, and thus raising the electron density on the central metal atom, the rate of the secondary reaction of cumene hydroperoxide is increased, leading to a faster rate of formation of 2-phenylpropan-2-ol:

$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot};\ RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}.$$

A multi-step mechanism has been reported also for the liquid-phase oxidation of isopropylbenzene and ethylbenzene in the presence of heterogeneous catalysts prepared by

depositing 8 wt. % of a Cu polychelate based on 4,4′-bis-(α-thiopicolinamido)biphenyl upon Al_2O_3.[37,38] The catalytic decomposition of the primary oxidation products (the hydroperoxides of ethylbenzene and isopropylbenzene) on the same polychelates is of zero order with respect to hydroperoxide and of first order with respect to the heterogeneous catalyst. E_{act} for the decomposition into radicals is 10.7 kcal mole^{-1} for ethylbenzene and 10.0 kcal mole^{-1} for isopropylbenzene[37].

Time-changes in the activity of the polychelate catalyst towards the formation of radicals from the hydroperoxide were examined by measuring initial rates (W_0) of consumption of 1-naphthol (an inhibitor for the resulting radicals) as a function of the time of operation of the catalyst. The rate of formation of radicals is high on a fresh catalyst, but falls off sharply after 20 min, and after 30 min it levels off at 25% of its initial value (Fig. 4). A comparison of the rates of formation of free radicals by thermal and by catalytic decomposition has shown that at 110°C the former (10^{-6} mole min^{-1}) is lower than the latter by a factor of $\sim 10^4$.[37]

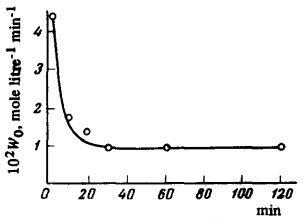
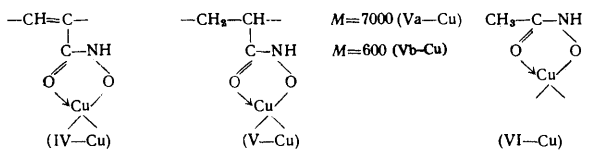


Figure 4. Change of W_0 with time at 90°C; [ROOH] = 3.26 wt. %, c_{cat} = 2.66 mg ml^{-1}.

From their study of the catalytic action of polychelates towards the liquid-phase oxidation of hydrocarbons the authors conclude that free radicals are formed mainly by the catalytic decomposition of the hydroperoxide, and the overall oxidation process is a classical non-branching chain reaction[39].

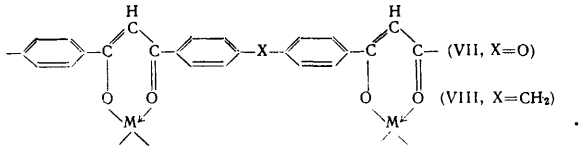
In 1966 a group of Japanese workers[40] prepared some new polychelates (hydroxamic acid derivatives) and studied their catalytic activity towards the decomposition of H_2O_2 in aqueous solutions. Thus, the following copper chelates of polyhydroxamic acid, with (IV) or without (V) a system of conjugated bonds (and Cl residues) in the main chain:



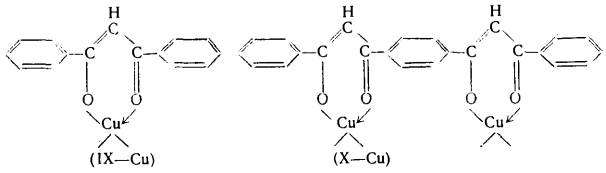
were compared for catalytic activity with the low-molecular-weight Cu chelate of methylhydroxamic acid (VI).

The catalytic activity of these chelates was found to increase in the sequence VI-Cu < Vb-Cu < Va-Cu < IV-Cu, in other words, it was found to be higher in the macromolecular chelates than in their low-molecular-weight analogue. The authors ascribe this behaviour to differences in the polarity of the copper–ligand bond[41].

The same workers[42] studied the catalytic activity of chelates of the poly-(β-diketone) type, which were prepared independently also by Soviet workers[43]:

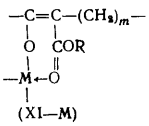


The catalytic activity of the polychelates VII-Cu and VIII-Cu for the decomposition of H_2O_2 is higher than that of their low-molecular-weight analogues IX-Cu and X-Cu



The rate of the decomposition reaction follows a first-order equation with respect to peroxide concentration; the catalytic activity of the chelates is fully reproducible on adding fresh portions of hydrogen peroxide. However, in respect of the catalytic activity of copper chelates of the β-diketone type towards the oxidation of L-ascorbic acid, the activity of the macromolecular chelates is higher than that of their low-molecular-weight analogues but the rate of oxidation shows a zero-order dependence on the concentration of ascorbic acid[42].

The present writers and coworkers[44] have examined the oxidase and catalase activity of a large number of transition metal complexes with macromolecular ligands of the poly-(β-ketoester) type first prepared by the ester polycondensation of dicarboxylic acid diesters[43,45]:



where m = 6, 7, 9; R = C_2H_5; M = Cu, Ni, Fe, Co, Mn.

The catalytic activity of these macromolecular chelates of poly-(β-ketoesters) towards the oxidation of ascorbic acid decreases in the order Cu > Ni ≫ Fe, Mn, Co (Fig. 5), whereas the opposite sequence of catalytic activity is observed in the decomposition of hydrogen peroxide by these complexes: Co > Mn > Fe ≫ Ni, Cu (Fig. 6). This inversion is ascribed to the mechanism of the interaction of the complexes with the substrates. Since the rate-limiting step in the decomposition of H_2O_2 under the influence of complexes is known[46] to be the addition of atomic oxygen, it is to be expected that complexes which are active in this step (and shift the equilibrium to the right) will have low activity in the O_2 absorption reaction which proceeds from right to left, as in the oxidation of ascorbic acid. We note that the catalytic activity of the complex XI-Co (m = 6) is increased very significantly by raising the pH to 10 (Fig. 6, curve *6*), as in the case of the decomposition of H_2O_2 in the presence of polycoordination complexes of type (III) (p.). The catalytic activity of macromolecular chelates of the poly-(β-ketoester) type (XI-M) is strongly dependent on the metal content, for example, copper (in the oxidation of ascorbic acid) or cobalt (in the decomposition of hydrogen peroxide), that is, on the degree of complex formation by the coordination centres (in both instances). As for the polycoordination compounds of

type (III) (p. 985), the catalytic activity of complexes with macromolecular ligands is very sensitive not only to the nature of the metal but also to the nature of the macromolecular ligand, for example, on the length of the polymethylene chain [m in the compound (XI-M)].[44]

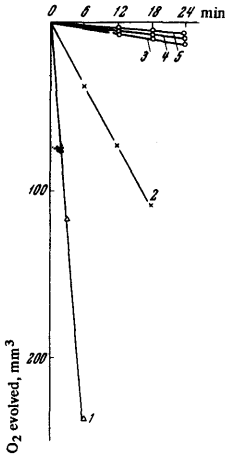


Figure 5. Kinetics of the oxidation of ascorbic acid in the presence of poly-(β-ketoester) complexes (XI)-M, m = 6: *1*) Cu, *2*) Ni, *3*) Mn, *4*) Co, *5*) Fe.

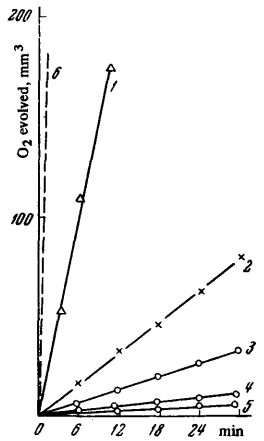
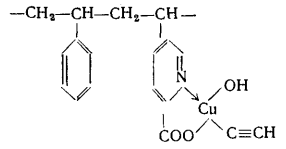


Figure 6. Kinetics of the decomposition of H_2O_2 in the presence of poly-(β-ketoester) complexes (XI)-M, m = 6: *1*) Co, *2*) Mn, *3*) Fe, *4*) Ni, *5*) Cu, *6*) decomposition in the presence of (XI)-Co at pH 10.

In our view, a quantitative comparison of the catalytic activity of macromolecular complexes with that of their low-molecular-weight analogues (such as the benzoyl- and acetyl-acetonates of the transition metals for VII-M, VIII-M, and IX-M), as Japanese workers[40,42], among others, have attempted, is complicated by the fact that these reactions proceed in a homogeneous medium in the presence of the low-molecular-weight complexes and in a heterogeneous medium in the presence of macromolecular chelates. This difficulty is apparent also with polymeric complexes of a different type—those of polymeric picolinic acid with copper (XII-Cu)—studied by Stepanov and Zosim[47] also in connection with the decomposition of hydrogen peroxide: under conditions of heterogeneous decomposition at room temperature the catalytic activity, expressed in mg-equiv. H_2O_2 per mg-equiv. Cu, is 204, whilst under homogeneous decomposition conditions it is 1540. We note, incidentally, that polymeric complexes of the same type were examined as catalysts for the synthesis of 1,4-butynediol from acetylene and formaldehyde. The copolymer of styrene and vinylpicolinic acid forms polymeric acetylide structures



(XII—Cu)

showing catalytic activity; the Cu complex of polypyridineethanol is practically unreactive towards acetylene under the same conditions. On the other hand the copper complex of the styrene–maleic acid copolymer, in which the copper atom is bound to the macromolecule by ionic forces only, catalyses the formation of butynediol on passing acetylene through a suspension of paraformaldehyde and of the polymeric acetylide[47].

A paper by Gregor and Liu[48] describes a study of catalysis on macromolecular zinc complexes obtained from poly-(*N*-vinylbenzimidazole). These workers investigated the decomposition of carbonic acid, and found that the "coefficient of catalytic activity" for this reaction (λ) is 400 ± 12 for both the Zn^{II} complex of poly-(*N*-vinylimidazole) and for poly-(*N*-vinylimidazole) itself, whereas for the monomeric imidazole λ is 1.5. Thus, the catalytic activity of the polymeric catalysts is significantly higher even for reactions of this type.

2. POLYMERISATION AND COPOLYMERISATION

Before beginning our discussion of the catalytic activity of the macromolecular chelates of transition metals towards the polymerisation of vinyl monomers, we shall dwell on a few examples of the use of low-molecular-weight chelates for the same purpose.

The earliest reports of the use of Co, Ni, and Fe acetylacetonates for the polymerisation and copolymerisation of unsaturated compounds appear in British patents of 1946;[49] subsequently, the use of ethylenediaminetetra-acetic acid complexes in emulsion polymerisation processes was also patented[50]. Later, Strubell[51] used a metal-containing oxidation–reduction system based on the propionylacetonate, benzoin, and benzoyl peroxide to initiate the polymerisation of methyl methacrylate. Fig. 7 shows curves for the increase of viscosity with time of the reaction mixture as a function of the metal in the propionylacetonate. The rate of polymerisation is directly proportional to the amount of added propionylacetonate with the exception of copper propionylacetonate, which activates the reaction strongly whatever amount is added, and of the nickel complex, which has no effect on the rate of polymerisation[51]. Indictor and Linder[52] have recently used a similar system (t-butyl hydroperoxide–acetylacetonate) to study the polymerisation of styrene at 50°C. They found that the initial rate of polymerisation is increased by adding $(1-2) \times 10^{-4}$

mole litre^{-1} of Co^{III}, Cr^{III}, Fe^{III}, or Cu^{II} acetylacetonate to the hydroperoxide, but begins to decrease at higher concentrations of these additives, possibly as a result of the formation of atomic oxygen. According to the authors, the acetylacetonates of other metals are inactive in this particular reaction.

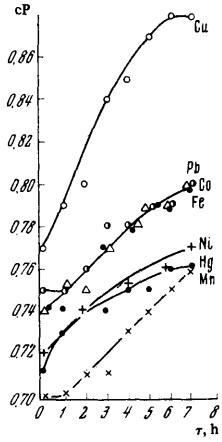


Figure 7. Viscosity of poly(methyl methacrylate) as a function of time of polymerisation in a benzoyl peroxide (1.210 g), benzoin (1.060 g), propionylacetonate (0.60 g) system.

Arnett and Mendelson[53] studied the polymerisation kinetics of styrene in the presence of a large number of acetylacetonates with and without benzoyl peroxide at 110°C, and obtained the following activity series for the metal acetylacetonates:

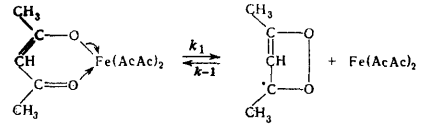
With peroxide: $Co^{III} \simeq Ce^{IV} > Mn^{III} > Fe^{III} > Al^{III} \simeq Cr^{III} \simeq$ without initiator $> V^{III}$.

Without peroxide: $Mn^{III} > Ce^{III} > Co^{III} > Fe^{III} > Al^{III} \simeq Cr^{III} \simeq$ without initiator $> V^{III}$.

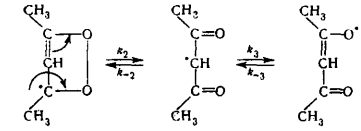
It is interesting to note that these catalytic activity sequences of the acetylacetonates for polymerisation are opposite to the thermal stability sequence obtained by Von Hoene and coworkers[54]:

$$Na^{I} > Cr^{III} > Al^{III} > Ni^{II} > Cu^{II} > Fe^{III} > Co^{II} > Co^{III} > Mn^{III}.$$

The last members of this series begin to decompose in an inert atmosphere at temperatures as low as 150°C, giving acetylacetone as the main decomposition product. Arnett and Mendelson were the first to try to explain the mechanism of formation of radicals on heating the acetylacetonates. Homolytic breaking of the chelate ring (for example, with Fe^{III}) takes place, with formation of Fe^{II} acetylacetonate and a free radical:



which can exist either in the C or in the O form and can initiate the polymerisation of styrene:



Bamford and coworkers[55] also made a study of the initiation of the polymerisation of vinyl monomers by low-molecular-weight metal chelates; they examined, in particular, systems containing the acetylacetonates of Cu^{II} and Co^{II}, and they pointed out that without suitable additives these systems are ineffective for the polymerisation of methyl methacrylate. In conjunction with halogenated compounds of the type CCl_4, CBr_4, CCl_3Br, CCl_3CN, $CCl_3.COONH_4$, and in particular with the last of these the copper chelate is fairly active at a concentration of 1.9×10^{-3} M at 80°C. The authors believe that at low concentrations of CCl_3COONH_4 ($< 6 \times 10^{-4}$ M) the initiating radical is formed by the decomposition of a 1:1 chelate–salt complex, whereas at high concentrations of CCl_3COONH_4 (2.5×10^{-2} M) the initiating radical is formed simply by the interaction of the chelate with the primary decomposition products of the salt[56].

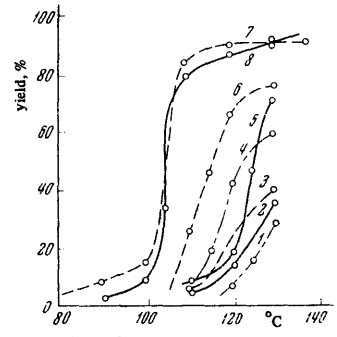


Figure 8. Polymerisation of styrene in the presence of acetylacetonates (concentration 0.5 wt. %, time 1 h):
1) Pd^{II}, *2*) Mn^{II}, *3*) Pt^{IV}, *4*) Ni^{II}, *5*) Rh^{IV}, *6*) Co^{III}, *7*) R_2O_2, *8*) Mn^{III}.

Kastning and coworkers[57] (see also the patents[58,59]) made a detailed study of the efficiency of initiation of the polymerisation of styrene by chelate complexes as a function of the nature of the central metal atom and of the structure of the ligand. It is evident from Fig. 8 that the highest yields of polystyrene are obtained by using the acetylacetonates of metals from Groups VII and VIII of the Periodic Table, and that the rates of polymerisation in the presence of the Mn^{III} chelate or of the peroxide are approximately equal. When the metal can exist in several valency states, the most effective initiators are those in which the metal exhibits the highest valency. The activity of chelates of 1,3-dicarbonyl compounds increases in the order dibenzoylmethane < benzoylacetone < acetylacetone < ethyl acetoacetate (Fig. 9).

Calvin and Wilson[60] showed that the stability constants (K_{st}) of Cu^{II} chelates increase in the same order.

One drawback of the acetylacetonates is the need to use relatively high polymerisation temperatures: these initiators were therefore activated by irradiation or by additives. Both in the presence and in the absence of activators the rate of polymerisation was proportional to the square root of the concentration of initiator[57].

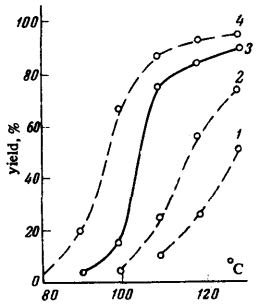


Figure 9. Polymerisation of styrene in the presence of Mn^{II} chelates (concentration 0.5 wt. %, time 1 h): *1*) dibenzoylmethane, *2*) benzoylacetone, *3*) acetylacetone, *4*) ethyl acetoacetate.

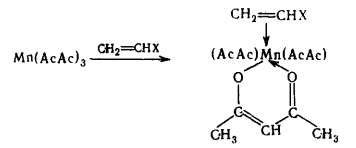
Chelate initiators can be used also for the polymerisation of acrylate and methacrylate esters, ethylene, butadiene, and for the copolymerisation of these monomers. Polymerisation of butadiene and isoprene under the influence of these chelates in solution yields high-molecular-weight polymers containing up to 60% of *cis*-1,4- and up to 10% of 1,2-vinyl units. A recent paper by Riches[61] on the polymerisation kinetics of dienes on Co^{III} acetylacetonate should be mentioned here: the reaction was found to be of one-half order with respect to the initiator and of first order with respect to the monomer (E_{act} = 13 and 20 kcal mole^{-1} for isoprene and butadiene respectively).

The results of Kastning and coworkers[57] on the copolymerisation of vinyl monomers which do not react under the influence of peroxides are particularly interesting. Thus, the polymerisation of a (1 : 1) mixture of styrene and vinyl acetate in the presence of Mn^{III} acetylacetonate at 80°C produces a copolymer containing 28 wt. % of vinyl acetate. (It is well known that for this pair of monomers r_1 = 55 and r_2 = 0.01.) At a higher temperature (100 to 150°C) and 1000–1600 atm pressure styrene and ethylene can be copolymerised with the same initiator. Simple vinyl ethers, which do not polymerise in the presence of chelates, can be made to copolymerise with ethylene to give up to 30% of vinyl ether units in the copolymer.

The authors do not put forward a mechanism for polymerisation in the presence of metal chelate initiators of the type examined, but some of their results are consistent with a free-radical mechanism. They were unable to observe any change in the valency of the central metal atom during polymerisation under the influence of chelates; valency changes took place only for reaction temperatures higher than the decomposition temperature of the chelate[57].

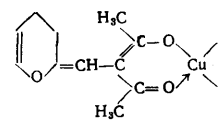
By using tracer atoms and infrared spectroscopy it was shown that the ligand is attached to the growing polymer chain; hence the authors concluded that the polymerisation can be initiated by free radicals formed from the chelate ligands. The microstructure of the resulting polymers does not depend on the nature of the ligand or of the activating additives, which affect only the rate of initiation, and the configuration of the chain is determined only by the nature of the central metal atom.

A group of Japanese workers[62] has measured the copolymerisation constants of vinyl monomers in the presence of metal acetylacetonates (Mn, Co, Fe). Thus, for the styrene–methyl methacrylate system they found r_1 = 0.53 ± 0.08 and r_2 = 0.52 ± 0.05, and for the styrene–methacrylate system r_1 = 0.89 ± 0.02 and r_2 = 0.17 ± 0.02. The authors believe that the first step in the polymerisation is decomposition by monomer attack¶, for example:



Nikolaev and coworkers have shown, in a very recent investigation[63], that their values for the copolymerisation constants of vinyl acetate and styrene (r_1 = 0.01 ± 0.1 and r_2 = 3.9 ± 0.8) suggest a change in the activity of the monomers and the radicals in the presence of $Mn(AcAc)_3$ as compared with copolymerisation in the presence of the usual radical initiators. The valency of manganese changes during the copolymerisation ($Mn^{III} \rightarrow Mn^{II}$), and the rate of the reaction decreases at the same time.

Whereas the above workers found copper acetylacetonate (without appropriate additives) to be inactive towards the polymerisation of vinyl monomers, Uehara and coworkers[64,65] have shown that unsaturated substituents in the pseudo-aromatic ring of Cu^{II} acetylacetonate enable it to initiate the polymerisation of styrene and methyl methacrylate (but not of vinyl acetate) at 0.5% concentration and 70°C. The polymerisation is inhibited by benzoquinone and is accelerated by ammonia and methanol. The reaction order is 0.5 with respect to the initiator and 1.8 with respect to the monomer; the overall activation energy is 20.1 kcal mole^{-1}. The infrared spectra suggest that the ligand becomes part of the polymer chain, as in the examples considered above. Initiators of this type (for example, XIII-Cu) have been used also to prepare a styrene–maleic anhydride (1 : 1) copolymer at room temperature:

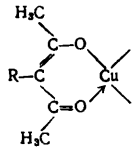


(XIII—Cu) .

We may assume that K_{st} for the (XIII-Cu) chelate, which is not quoted by the authors, is lower than K_{st} for the unsubstituted acetylacetonate, because of conjugation of the chelate ring with the π-system of the dihydropyran ring: we may ascribe the catalytic activity to this effect. The same workers[65,66] have demonstrated the influence of other substituents with double bonds on the activity of substituted copper acetylacetonates in polymerisations. They condensed acetylacetone with propionaldehyde, butyraldehyde,

¶ Subsequently, the reaction proceeds by the schemes shown on p.989.

isobutyraldehyde, and dimethacrolein, and obtained (XIV-Cu)



(XIV—Cu)

where R = CH= (*a*); CH=CH—CH_3 (*b*); CH=CH—CH_2CH_3 (*c*); $CH=C(CH_3)_2$ (*d*); or its hydrogenation products $CH_2CH_2CH_3$ (*e*); $CH_2CH_2CH_2CH_3$ (*f*).

The following activity sequences are given for the XIV-Cu chelates: $a > b > c > f > d > e \simeq 0$ for styrene; $a > c > b > d > e > f \simeq 0$ for methyl methacrylate.

In 1965 Bamford and Lind[67] published the results of a study of the initiation of polymerisation with acetylacetonates without any additives. In contrast to Kastning's results[57], obtained for the polymerisation of styrene at 100°C, these authors (who studied the polymerisation of methyl methacrylate at 80°C) arranged the acetylacetonates examined in their work in the following order: $Mn^{III} > Ni^{II} > V^{III} > Cr^{III} \gg Co^{III} > TiO^{II} > Pb^{II}$. Neither addition of CCl_3COONH_4 (2.77×10^{-4} M) up to a chelate concentration of 2.7×10^{-3} M, nor addition of equimolecular amounts of CCl_4 up to a chelate concentration of 2.8×10^{-2} M, produced any increase in the reaction rate. A more detailed kinetic analysis of a system containing Mn^{III} acetylacetonate (curve *3* of Fig. 10) showed that the rate of polymerisation is proportional to the concentration of chelate raised to the power 1/2:

$$\omega = 1.0 \cdot 10^{-2} [Mn(AcAc)_3]^{1/2} \text{ mole litre}^{-1} \text{ s}^{-1} \text{ (at 80°C)},$$
$$\omega = 0.05 \cdot 10^{-2} [Mn(AcAc)_3]^{1/2} \text{ mole litre}^{-1} \text{ s}^{-1} \text{ (at 70°C)}.$$

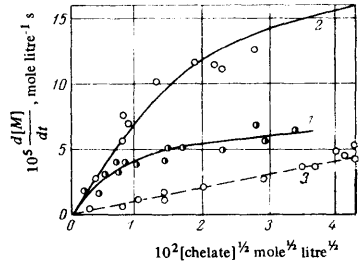


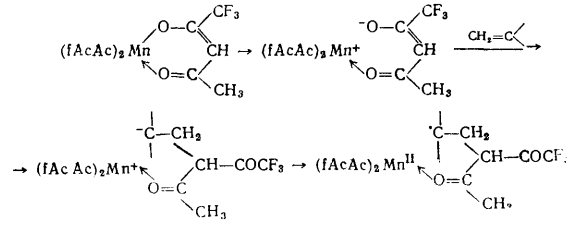
Figure 10. Polymerisation of methyl methacrylate at 80°C on: *1*) Mn^{III}-*p,p'*-dichlorodibenzoylmethane; *2*) Mn^{III} acetylacetonate without additives; *3*) ditto, with CCl_4.

The product $k_p k_t^{-1/2}$ (rate constants for chain propagation and chain termination respectively) is close to the known value for the free-radical polymerisation of methyl methacrylate (0.17 $\text{mole}^{-1/2}$ $\text{litre}^{-1/2}$ $\text{s}^{1/2}$). Hence the authors conclude that polymerisation occurs by a free-radical mechanism in the present system under the influence of radicals formed by the decomposition of the chelate. A similar hypothesis had been put forward by Arnett and Mendelson[53] (see p. 989).

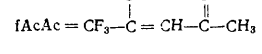
The rates of polymerisation on Mn^{III}-dibenzoylmethane and its *p,p'*-dichloro-derivative (Fig. 10) are proportional to the concentration of the chelate to the power 1/2 for low chelate concentrations ($< 10^{-4}$ M for curve *1* and $< 0.4 \times 10^{-4}$ M for curve *2*). At higher chelate concentrations ($> 10^{-3}$ M) this relationship no longer applies and the product $k_p k_t^{-1/2}$ takes abnormally low values (0.14 and 0.13 $\text{mole}^{-1/2}$ $\text{litre}^{-1/2}$ $\text{s}^{1/2}$ respectively), pointing to some unexplained type of inhibition. Another paper by Bamford and Lind[68], devoted to the selective initiation of free-radical polymerisation in fluorinated derivatives of acetylacetonates, is particularly interesting. In the case of the fluorinated derivative of Mn^{III} acetylacetonate the rate of polymerisation of methyl methacrylate at 80°C is higher by a factor of 7 than the rate corresponding to the non-fluorinated analogue. On the other hand, the polymerisation of styrene is substantially inhibited in the presence of this system: for a given concentration of the fluorinated and the non-fluorinated acetylacetonate (2.5×10^{-4} M), the rates of formation of the polymer are 1.6 and 34 mole litre^{-1} s^{-1} respectively. This inhibition is explained by the fast interaction of the styrene radicals with Mn ions (positively charged) induced by the CF_3 group. The ratio of the rates of polymerisation initiated by benzoyl peroxide in the presence (W) and in the absence (W_0) of the chelate is given by the equation

$$W/W_0 = (Ik_t)^{1/2}/b[C] + a/b \quad (k'/I)^{1/2},$$

where C is the chelate concentration, I is the rate of polymerisation initiated by benzoyl peroxide, a and b are constants which characterise the rates of initiation and of inhibition of the reaction by the chelate. Comparison of the data on the polymerisation of methyl methacrylate and of styrene shows that the action of the fluorinated acetylacetonate of Mn^{III} is highly selective: it induces most effectively the polymerisation of monomers having a strongly polarised double bond. In particular, the rate of polymerisation of acrylonitrile is 70 times higher in the presence of this compound than in the presence of the corresponding acetylacetonate. This is ascribed to the ready attachment of a monomer with relatively high electron-accepting properties to the anion formed by the cleavage of the Mn—O bond. This anion subsequently decomposes with formation of a radical and of the Mn^{II} chelate. The proposed initiation mechanism is consistent with the extremely low (2×10^6 litre mole^{-1} s^{-1}) frequency factor observed in the polymerisation of methyl methacrylate in the presence of the fluorinated chelate:



where

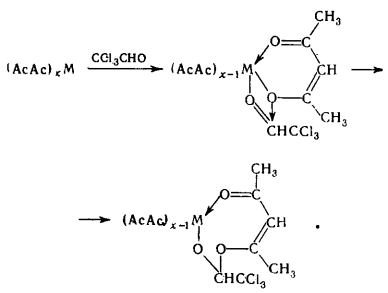


We note that the strong inductive effect of the CF_3 group in $CF_3COCH_2COCH_3$ is responsible for the much lower value of K_{st} of its chelate as compared with the acetylacetonates[26] (see p. 990).

The work of Bamford and Lind[68] provides one of the few examples of selective radical (or, more strictly, radical-ionic) polymerisation processes. We may conclude from this work that a correct choice of the structure of the low-molecular-weight or macromolecular ligand allows the free-radical nature of the process to be retained whilst

adopting some features of the ionic mechanism, thus giving rise to a polymerisation which is intermediate between radical and ionic polymerisation. Thus, under conditions of radical polymerisation it becomes possible to vary the reactivity both of the monomer and of the resulting radical. It may be suggested that the use of chelate complexes is the most efficient way of influencing the reactivity of the radical both in the initiation and in the chain propagation step. In this sense, both the low-molecular-weight and the macromolecular chelates offer interesting possibilities because of the ease of electron transfer in the ligand and of the change in electron density on the metal in the coordination centre.

An interesting example of selective initiation of polymerisation by acetylacetonates of the transition metals Mn^{II} and Mn^{III}, Co^{II} and Co^{III}, was reported by Otsu and coworkers[69]. The polymerisation of chloral, according to these authors, follows a coordination-anionic mechanism according to the scheme



The authors have shown that acetylacetonates of this type can initiate the polymerisation not only of chloral but also of acetaldehyde and of styrene oxide. (The polymerisation of formaldehyde by acetylacetonates had already been disclosed in the patent literature[70].)

In contrast to the views of Kastning[57] and of Bamford[67] (see p. 991), Otsu and coworkers[69] believe that acetylacetonates of metals in both the upper and the lower valency state of the metal can initiate the polymerisation of methyl methacrylate as well as of chloral.

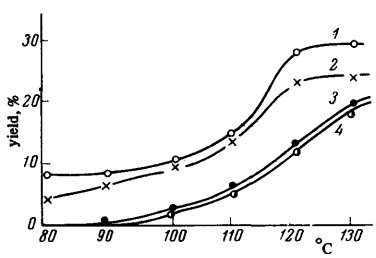
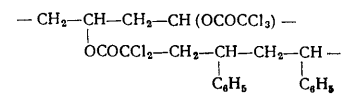


Figure 11. Temperature dependence of the yield of polymerisation products of styrene on poly-(β-ketoester) complexes, (XI)-M, $m = 6$. Time 1 h, concentration of complex 1 wt.%:
1) Co, *2*) Mn, *3*) Ni, *4*) no complex.

The macromolecular chelates of the poly-(β-keto-ester) type XI-M described by the present writers[43-45,71] were found to initiate the polymerisation of vinyl monomers, such as styrene, methyl methacrylate, etc. Fig. 11 shows the temperature dependence of the degree of conversion of styrene in the presence of various macromolecular chelates of this type. Only the Co and Mn macromolecular chelates are catalytically active under the stated conditions; the degree of conversion in the presence of the Ni chelate is practically the same as in the absence of the chelate. We note that according to Kastning and coworkers[57] the low-molecular-weight chelates of Co and Mn are also the most active in the initiation of the polymerisation of styrene. The rate of block polymerisation of styrene at 80°C in the presence of the manganese chelate (XI-Mn) depends linearly on the concentration of the chelate; addition of benzoquinone (0.2 g litre^{-1}) destroys the polymerisation effect. It was shown that as well as initiation of the reaction, grafting of polystyrene units to the macromolecular initiator (XI-Mn) takes place. The resulting graft copolymers lose their metal atoms as a result of treatment with dilute mineral acids, and become soluble in organic solvents (possibly through the collapse of the three-dimensional network of the initiator macromolecule), whilst retaining the chemical bond between the grafted chain and the macromolecular ligand. When the polymerisation of butadiene was initiated by the poly-(β-diketone) chelates (XI-Mn) and (XI-Co), a significant increase in the yield of polymers can be demonstrated (as compared with initiation by the appropriate acetylacetonates); the product consists of a graft copolymer of butadiene and the poly-(β-ketoester). The degree of grafting of polybutadiene to the macromolecular chelate is 0.80–0.93; the structure of the polybutadiene chains, which contain 20, 34, and 46% of 1,2-, 1,4-*cis*-, and 1,4-*trans*- respectively, is characteristic of polybutadiene prepared by radical initiation.

It is interesting to note that graft (or block) copolymers were obtained by Bamford and coworkers[72] by a different method, namely, by the polymerisation of styrene under the influence of metal carbonyls or acetylacetonates in the presence (as activating additives, see p. 989) of high-molecular-weight halogen compounds, such as poly(vinyl trichloroacetate):



To conclude this Section we note that the catalytic properties of polycoordination polymers (of the quinizarine type) towards the polymerisation of styrene were reported as early as in 1963,[73] but neither the reaction nor the polymerisation products were investigated.

3. CATALYTIC ACTIVITY AND STRUCTURE OF MACROMOLECULAR CHELATES

Whereas the relationship between catalytic activity and structure of low-molecular-weight chelates has been adequately discussed in the literature (see review by Schrauzer et al.[74]), relatively little has been published on this problem regarding macromolecular chelate compounds. Roginskii and his coworkers studied the catalytic activity of semiconductors (for example, polyphthalocyanines) in decompositions and oxidations, and they concluded that the catalytic activity of semiconductors is determined by collective electrical properties[75]. The importance of the collective electrical properties of the system was stressed also by Inoue and coworkers[15,16], who studied the catalysis of the oxidation of the ethyleneacetal of acetaldehyde on mixed polyphthalocyanine semiconductors.

Min'kov and Keier[76] specially pointed out the change in the activity of the catalyst during the reaction in their study of the mechanism of the liquid-phase oxidation of isopropylbenzene on low-molecular-weight copper phthalocyanine chelates. They concluded that initiation in the case of copper phthalocyanine does not involve the activation of oxygen but rather the catalytic decomposition of the reaction products of α-cumyl hydroperoxide into free radicals, which proceeds unimolecularly with specific rate constant $k_{sp} = 1.5 \times 10^3 \exp(-13\,200/RT)$ s^{-1} at 40–70°C and bimolecularly with $k_{sp} = 3.6 \times 10^{10} \exp(-24\,600/RT)$ litre $mole^{-1}$ s^{-1} at 90–100°C. Thus, the decomposition of the hydroperoxide occurs by different mechanisms, depending on the temperature. The activity of the catalyst in this reaction varies with time: at 101°C the rate of decomposition of the hydroperoxide decreases by a factor of 2.5 during the first two hours, and then remains constant, but at 60°C the rate of decomposition of the hydroperoxide has not reached a steady value even after 8.5 h (see Fig. 12).

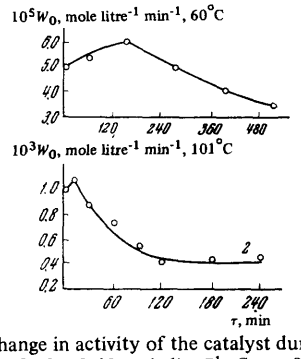


Figure 12. Change in activity of the catalyst during the reaction: *1*) at 60°C, [ROOH] = 0.40 mole litre^{-1}, C_{cat} = 0.66 mg ml^{-1}; *2*) ditto, at 101°C.

On the basis of X-ray diffraction, ESR spectra, and infrared spectra it has been shown that the change in activity of Cu phthalocyanine is associated with a change in the crystal structure of the material (transformation from the α- to the β-modification). As regards the nature of the interaction between the hydroperoxide and the phthalocyanine, the data show that there is no direct interaction between the hydroperoxide and the copper ion: the interaction is with the whole of the π-electron system of the ligand. However, the phthalocyanine itself (metal-free) is inactive towards this reaction. The copper ion exerts a strong polarising effect on the ligand, increasing the π-electron density on the nearest nitrogen atoms and decreasing it on the nitrogen atoms remote from the metal. It is the lower density of π-electrons on the nitrogen atoms not involved in the chelate ring which favours complex formation with the hydroperoxide and activates it in reactions involving its decomposition into free radicals, which finally bring about the oxidation of cumene[77].

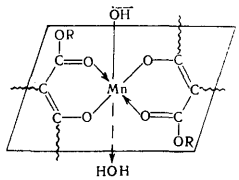
Keier and coworkers[25,35] tried to explain the change in rate of a reaction (for example, the decomposition of hydrazine) on low-molecular-weight complexes of different purity, obtained by recrystallisation. By studying ESR spectra they concluded that crystallisation increases the degree of order of the crystal structure. Polymeric chelates with a more ordered structure also showed a lower reactivity towards the reaction under study. For example, a polychelate with a highly ordered structure which was almost free from defects and planar was similar to its low-molecular analogues in reactivity. This material, prepared in a nitrogen atmosphere, was characterised by a narrow ESR line and by well developed anisotropy[39]. ESR spectral studies before and after vacuum annealing showed that polychelates with a regular structure are not formed under the preparative conditions used. Ordering of the polymer structure takes place during the heat treatment, involving completion of the complex formation and molecular redistribution, and also exchange interaction between the copper ions resulting from the increased conjugation in the polymer. The tetrahedrally distorted structure of the chelate centre becomes planar, and the molecular weight of the polychelate increases. Mutual interconversion of various modifications of the polymer is also possible. All these factors tend to lower the reactivity of the polychelate[39].

The surface of the polychelates plays a well known role in determining their catalytic activity. Thus, the catalytic activity per unit weight of polymer increases by almost two orders of magnitude on increasing the surface area of copper polychelates based on α-thiopicolinamidobiphenyl[34]. In an investigation of the catalytic activity of polychelates towards the decomposition of N_2H_4 it was shown that the chelate suffers fully or partly irreversible changes. Measurements of the decrease in intensity of the ESR signal at the beginning of the reaction give almost quantitative agreement between the number of copper chelate centres which have reacted and the number of decomposed N_2H_4 molecules. The first step of the reaction may consist in the attachment of the reactant to the metal of the chelate centre, accompanied by an electron transfer which alters the charge on the metal and thus weakens the metal–ligand bond[25].

Elimination of the ligand can then take place, with simultaneous attachment of hydrogen atoms at the broken bonds and evolution of NH_3 and H_2 molecules into the gas phase. However, the breakdown of the chelation centre is complete when the copper is reduced to Cu^0, with further increase in the rate of decomposition of the substrate. (The rate of decomposition after 21 h increases to 3 cm^3 h^{-1} as compared with 0.1 cm^3 h^{-1} during the first hour.) In the oxidation of isopropylbenzene (p. 986) the polychelates also react with the substrate and undergo irreversible changes, however (and in contrast to the previous reaction) the deactivation of the catalyst is much slower. Thus, polymeric chelates take part in the formation of free radicals as true heterogeneous catalysts[36].

In order to identify the type of metal–polymer bond and the valency state of the metal in the chelates with macromolecular ligands (XI-M) prepared by the present writers, their magnetic moments μ_{eff} were measured[78]. The μ_{eff} values (in Bohr magnetons) were 3.83 and 4.87 respectively for different samples of XI-Mn, which corresponds to three and four unpaired d-electrons. Thus, the samples were spin-free and contained Mn^{IV} and Mn^{III} ions. It is not easy to envisage a coordination of three (or four) macromolecular ligands around the central manganese atom, as the Stewart–Briglebb molecular model clearly shows. Hence we may imagine that the manganese atom is surrounded by six oxygen atoms, four of which belong to polymeric ligands and the other two to two hydroxyls (for Mn^{IV}) or to one

hydroxyl and one solvent water molecule (for Mn^{III}), which thus complete the coordination octahedron:



Some of the centres may be coordinated to one macromolecular ligand and two solvent water molecules[71].

In this instance, as with the macromolecular chelates of type (III),[34] the high catalytic activity can be ascribed[78,79] to the formation of disordered, incompletely saturated coordination centres in the polymer chain, with a distorted geometrical configuration.

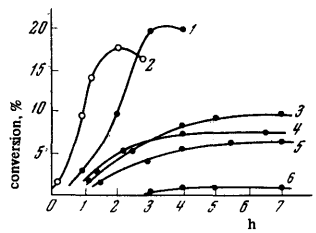


Figure 13. Liquid-phase oxidation of acrolein in the presence of the following acetylacetonates:
1) Mn, *2*) Co, *3*) Fe, *4*) Cu, *5*) Ni, *6*) acetylacetone; concentration 1×10^{-3} mole litre^{-1}.

Japanese workers have put forward[80] some interesting ideas on the changes in the coordination centre of the catalyst in the course of the catalytic reaction. The activity of acetylacetonates decreases in the series Co > Mn ≫ Fe ≃ Cu > Ni (Fig. 13) for the liquid-phase oxidation of acrolein to acrylic and peracrylic acid, and acrylic acid polymers. (The solvent used for the oxidation determines the relative yield of these products.) The authors believe that the reaction occurs by a radical mechanism, and that the initial and the final products (including polymeric products) enter into the coordination centre of the catalyst (for example, Co^{III} acetylacetonate) as they are formed.

The most important thermodynamic characteristic of complexes in general (and macromolecular complexes in particular) is their so-called stability (or instability) constant. Thus, according to Kenney[81], K_{st} of polycoordination polymers (that is, the equilibrium constant of the reaction $M^{m+} + mA^- \rightleftharpoons [MA_m]$) is a measure of the free energy change attending complex formation. The values of this constant for bivalent metals increase in the series Mg < Mn < Fe < Co < Ni < Cu < Zn.[81] Thus, it is particularly relevant to establish the dependence of the activity of macromolecular chelates upon their stability—for example, for the complexes of the 2(O, O) type considered here. The Japanese workers already mentioned[40,42] observed a correlation between the catalytic activity series of the poly-(β-diketone) copper chelates (see p. 987), VII-Cu > VIII-Cu > IX-Cu > X-Cu, and the shifts of the absorption maxima in the visible region of the spectrum towards longer waves (λ_{max} 388, 375, 370, 368 mμm respectively). This is evidence that the energy of the electronic transitions in the macromolecular ligands and their chelates decreases in the stated order, and therefore the strength of the bond between the macromolecular ligand and the metal must also decrease in the same order.

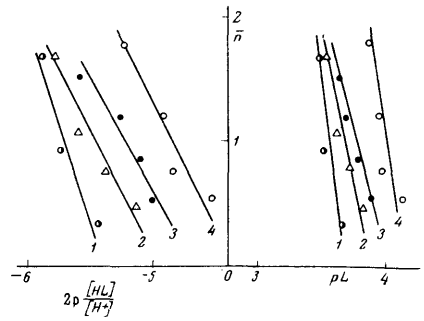


Figure 14. Curves for the formation of poly-(β-ketoester) complexes, (XI)-M, $m = 6$:
1) Mn, *2*) Co, *3*) Ni, *4*) Cu.

The present writers and their coworkers[82] have measured the acid–base dissociation constants of the macromolecular ligands of the poly-(β-ketoester) type XI and the formation (or stability) constants of their complexes with transition metal cations. The acid–base dissociation constant K_a of the macromolecular ligand (XI, $m = 6$) was found to be $10^{-6.4}$ (that is, $pK_a = 6.4$). This value was obtained from the Henderson–Hasselbach equation $pH = pK_a - n\lg[(1 - \alpha)/\alpha]$, where α is the degree of neutralisation, and n is a constant independent of the extent of polymerisation whose value varies between 1 and 2 and increases with dilution of the solution. The formation constants (or stability constants) of the macromolecular chelates XI-M decrease in the series Cu > Ni > Co > Mn (Fig. 14). We note that the same sequence also describes the increase in catalytic activity of the poly-(β-ketoester) complexes XI-M for the decomposition of hydrogen peroxide, and the decrease in the activity of these complexes for the oxidation of ascorbic acid (see Figs. 6 and 5 respectively, and p. 987).

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Published data show that the field of macromolecular complexes is an interesting one from many viewpoints. Leaving aside the problem of preparing thermally stable polychelates[83], it is obvious that macromolecular complexes are vitally important as catalytic systems which are active towards a wide range of reactions including the polymerisation of vinyl monomers.

These systems are interesting also from the standpoint of structural studies, since their structure allows mutual interaction of coordination centres through the polymer chain.

Macromolecular complexes containing metals can be treated as model compounds for the substances which take part in a number of biochemical processes, such as the assimilation of metal ions (Cu, Fe), the blocking of functional groups (Mn), redox reactions of the cell (Cu, Fe, Co), and others[84].

Each of the two main classes of macromolecular complexes, prepared either by polycoordination of multivalent ions with multidentate low-molecular-weight ligands or from previously synthesised macromolecular ligands, has some advantages as a catalytic system: the former because of the presence of a conjugated system and of the concomitant synergic effect (that is, the collective electronic property of the macromolecule), the latter because of the presence of a macromolecule which is not destroyed by the removal or replacement of some metal atoms by others, and also because of the solubility of the initial macromolecular ligand.

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The Inhomogeneity of Copolymers with Respect to Composition

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The inhomogeneity of composition (i.c.) which arises in copolymerisation not only influences the physical and physicochemical properties of the copolymers formed but also, when it is correctly assessed, makes it possible to arrive at certain conclusions concerning the copolymerisation mechanism. The review deals mainly with binary statistical copolymerisation. A critical analysis is given of the "classical" Mayo-Lewis concept, according to which the copolymerisation constants remain unchanged throughout the process. Regarding such systems as "normal" or standard, the authors have derived expressions for their distribution functions with respect to composition. Further it is noted that the case where r_1 and r_2 are constant is more likely to be an exception rather than the rule and possible causes of the departure from such constancy are indicated. The principles of the derivation of the integral and differential distribution functions with respect to composition for copolymerising systems are discussed in detail. Analytical expressions are proposed for numerical estimates of inhomogeneity with respect to composition. In their statistical significance the expressions obtained resemble equations of different degrees governing the molecular weight ratios in homopolymerisation. The deviations from the "norm" in the copolymerisation of ionogenic monomers in aqueous solution are considered as an example of the application of these expressions. In this case the copolymerisation constants depend on the conversion due to the changes in the degree of ionisation of the "bound" monomers compared with the free monomers and due to the overall change in ionic strength. In conclusion a critical analysis is given of the existing experimental methods for the determination of inhomogeneity of composition and the prospects for the further development of the statistical theory of copolymerisation are discussed. The bibliography includes 111 references.

CONTENTS

I. Introduction 996
II. The causes of inhomogeneity of composition 997
III. Integral and differential curves for distribution with respect to composition 999
IV. Analysis of the chemical structure of copolymers 1003
V. Quantitative estimate of the inhomogeneity of copolymers with respect to composition 1005

I. INTRODUCTION

The polydispersity of copolymers is not restricted to differences in chain length. Individual macromolecules can differ also in their chemical composition (inhomogeneity of composition) or in their shape (molecular polymorphism)[1,2]. All three types of polydispersity are a consequence of certain processes occurring in copolymerisation. Their analysis may provide valuable information about the kinetics and mechanism of copolymerisation—by analogy with the detailed information about the homopolymerisation mechanism derived from the analysis of molecular weight distribution (m.w.d.). In addition, inhomogeneity of composition and molecular polymorphism have a

significant effect on the macroscopic properties of copolymeric materials—to a greater extent than the molecular weight distribution.

Nevertheless in the extensive literature devoted to the problems of copolymerisation the number of papers dealing with different types of polydispersity, in particular inhomogeneity of composition, is relatively small[3]. To a large extent this is because as a rule all three types of polydispersity in copolymers are present at the same time and molecular polymorphism is usually a consequence of inhomogeneity of composition[2], which has different effects at the level of macromolecular (in solutions) and supermolecular (in the solid) structures. Not only are there no generally accepted "specific" methods "designed" for a particular type of polydispersity, but also there exists no adequate statistical theory which would describe inhomogeneity of composition, or molecular polymorphism, with the aid of distribution functions or their moments, by analogy with molecular weight distribution[2,4]. Therefore the relatively reliable individual items of evidence concerning inhomogeneity of composition and molecular weight distribution have been obtained only for certain model copolymeric systems.

To avoid the above difficulties, the great majority of investigators have confined themselves to the calculation of the apparent copolymerisation constants r_1 and r_2,[5-10] assuming *a priori* that the system obeys the Mayo–Lewis equation[11-13]. However, as will be shown below, this equation describes the actual copolymerisation process only to a first approximation and is by no means applicable to any system. There exist many "unusual" systems (systems which do not obey the Mayo–Lewis equation), the mechanism and kinetics of the copolymerisation of which cannot be characterised solely by the information concerning the average composition of the copolymer $\bar{\alpha}$ (see below) for certain fixed conversions ψ and compositions of the initial monomer mixture (substrate). In order to characterise such systems, it is essential to have detailed information about their inhomogeneity with respect to composition.

The present review deals with modern hypotheses concerning the causes of inhomogeneity of composition and rational quantitative methods for the statistical description of this inhomogeneity are discussed as well as special experimental methods and principles "designed" specifically for inhomogeneity of composition. The review is concerned mainly with two-component statistical copolymers, since this class of systems has been most thoroughly investigated. However, with some stipulations, the postulates developed below may be extended also to heteropolymers (block and graft polymers) and to multicomponent systems.

II. THE CAUSES OF INHOMOGENEITY OF COMPOSITION

In the estimation of inhomogeneity of composition one should always bear in mind that it is in general due to two fundamentally different processes. Firstly, inhomogeneity of composition is a consequence of the statistical nature of the copolymerisation process itself. We shall call this type of inhomogeneity "instantaneous" inhomogeneity of composition (i.i.c.). The second type of inhomogeneity (we shall call this the "conversion" inhomogeneity of composition, c.i.c.) is caused by macroscopic changes in the parameters of the reaction medium during copolymerisation. In the simplest case conversion inhomogeneity is due to the changes in the composition of the substrate during copolymerisation. Henceforth in the discussion of the inhomogeneity of the composition of copolymers it will be understood that instantaneous and conversion inhomogeneity are present. We shall discuss in greater detail the causes of both types of inhomogeneity.

1. "Instantaneous" Inhomogeneity of Composition

The macroscopic copolymerisation process is a consequence of the superposition of a multiplicity of elementary reactions, such as the initiation and propagation of the kinetic chain, different types of chain transfer, termination of the kinetic chain (by recombination and disproportionation mechanisms), etc.[1,2]. Individual elementary processes in the formation of copolymer macromolecules are also of a statistical character and therefore at each given instant the entire homogeneous system exhibits microheterogeneity due to local fluctuations in the concentrations of the reactants. This is ultimately responsible for "instantaneous" inhomogeneity of copolymers both with respect to molecular weight and composition. Distribution functions with respect to molecular weight and composition α have been obtained in an analytical form for two-component copolymeric systems—by Simha and Branson[14] in a simplified form and more rigorously by Stockmayer[15]. Let $w_{n,\alpha}$ be the weight fraction of macroradicals with a degree of polymerisation n and the composition $\alpha = [A]/([B] + [A])$, where [A] and [B] are the molar concentrations of components A and B in the macroradical (their concentrations in the substrate are denoted respectively by [a] and [b]), and $\alpha = \alpha_0 + \Delta\alpha$, where $\alpha_0 = \sum_{i=1}^{k} N_i\alpha_i / \sum_{i=1}^{k} N_i$ is the arithmetical mean composition of the statistical ensemble of k macroradical fractions and N_i is the number of macroradicals with the composition α_i.

If [a] = const., [b] = const., and $n \gg 1$, then under quasi-steady-state conditions

$$w_{n,\alpha} = A\, n^{1/2} e^{-n(\Delta\alpha)^2/D} e^{-n/B}. \qquad (1)$$

Here $B = \sum_{p=1}^{m} N_p n_p / \sum_{p=1}^{m} N_p$ is the arithmetical mean (number average) degree of polymerisation of macroradicals,

$$A = \frac{\sum_{p=1}^{m} N_p}{\sum_{p=1}^{m} N_p n_p^2} \left[\frac{r_A [a]^2 + 2[a][b] + r_B [b]^2}{2\pi\alpha_0 (1-\alpha_0)(r_A [a]^2 + 2r_A r_B [a][b] + r_B [b]^2)} \right]^{1/2},$$

$$D = 2\alpha(1-\alpha_0) \frac{r_A [a]^2 + 2r_A r_B [a][b] + r_B [b]^2}{r_A [a]^2 + 2[a][b] + r_B [b]^2},$$

and r_A and r_B are copolymerisation constants.

As was to be expected from the very formulation of the problem, the distribution function with respect to composition depends significantly on the molecular weight distribution of the macroradicals. To establish an unambiguous relation with n (or α), Eqn. (1) must be integrated with respect to all the α (or n). Integration yields

$$w_\alpha = \frac{3}{4} \left(\frac{B}{D} \right)^{1/2} \left[1 + \frac{B}{D} (\Delta\alpha)^2 \right]^{-5/2} \qquad (2a)$$

and

$$w_n = \frac{n \sum_{p=1}^{m} N_p n_p^2}{\sum_{p=1}^{m} N_p} e^{-n/B}. \qquad (2b)$$

It is easy to show that Eqn. (2b) can be reduced to the "most probable" [2] distribution function with respect to molecular weight for homopolymeric systems [16].

We may note that an expression analogous to Eqn. (1) can be obtained also when a different aspect of the copolymerisation process is examined. The macroradicals formed may be regarded as chain fragments which arise from a finite number of breaks in a quasi-infinite Kuhn chain [2,17], which is ordered with respect to composition. One should remember that all the distribution functions considered [Eqns. (1), (2a), and (2b)] were derived for "instantaneous" values of [a] and [b], time not entering into them, and therefore it is impossible to obtain $w_{n,\alpha}$ in an explicit form by means of Eqns. (1), (2a), and (2b) for finite values of ψ. Eqns. (1), (2a), and (2b) were obtained for the condition $n \to \infty$, and become significantly more complex when they are modified to describe the instantaneous inhomogeneity of composition in real systems [18]. Thus if Eqn. (1) is valid also for finite n under the condition that the termination of kinetic chains takes place only by a disproportionation mechanism, then, with the probability f of recombination termination steps, Eqn. (1) becomes

$$\omega_{n,\alpha} = A\left(1 - f + \frac{nf}{B}\right) n^{1/6} e^{-n/B} e^{-n(\Delta\alpha)^2/D} . \qquad (3)$$

Experimental tests of Eqns. (1), (2a), (2b), and (3) require a precision in the estimation of the composition of the copolymer which is not a present attainable. However, the contribution of instantaneous inhomogeneity to the total inhomogeneity of composition should not be overestimated —for copolymers with $n > 500$ the broadening of the curve for inhomogeneity of composition due to instantaneous inhomogeneity is relatively slight and decreases with increasing n.

Instantaneous inhomogeneity of composition can also be a consequence of the microheterogeneity of the system in the following cases.

1. The formation around the macroradicals of a "microsubstrate" with the composition [a]′/[b]′ which differs from the macroscopic value [a]/[b] and depends on n [2].

2. The dependence of the reactivity of the co-monomers on n arises from the possible dependence of the diffusion coefficients of the monomers on microviscosity in the bulk of the macroradicals. A change in the conformation of the macroradicals during copolymerisation (i.e. the occurrence of molecular polymorphism) should favour the appearance of additional instantaneous inhomogeneity of composition.

3. A change in the nature of the selective interactions between the co-monomers and the individual components in the copolymerising system [19].

The effect of each component of instantaneous inhomogeneity of composition can be taken into account only by means of appropriate model experiments and it is necessary to attain a very high accuracy in the determination of α.

2. Conversion Inhomogeneity of Composition

Systems which obey the Mayo–Lewis rule. The Mayo–Lewis equation was derived on the following assumptions:

(1) [a] = const. and [b] = const.;
(2) $r_A \neq r_A(t)$ and $r_B \neq r_B(t)$.

It is assumed that the reactivity of the monomer is independent of the alternation of the preceding units up to the terminal radical.

(3) $r_A \neq r_A(n)$ and $r_B \neq r_B(n)$;
(4) $r_A \neq r_A([a]/[b])$ and $r_B \neq r_B([a]/[b])$;
(5) the reaction system is fully homogeneous;
(6) the chain propagation reactions are completely irreversible.
Then

$$\frac{[A]}{[B]} = \frac{[a]}{[b]}\left\{\frac{r_A[a]+[b]}{r_B[b]+[a]}\right\} . \qquad (4)$$

It is possible to modify this expression. We introduce the weight concentrations (g cm^{-3}) of the substrate components C_A and C_B defined by the equations

$$[a] = \frac{C_A/M_A}{C_A/M_A + C_B/M_B} \text{ and } [b] = \frac{C_B/M_B}{C_A/M_A + C_B/M_B},$$

where M_A and M_B are the molecular weights of the components A and B. Eqn. (4) can then be written in the more convenient form:

$$\frac{M_A}{M_B}\frac{\beta^2}{\gamma} r_B - r_A = \beta\left(\frac{M_A}{M_B} - \frac{1}{\gamma}\right), \qquad (5)$$

where $\gamma = dC_B/dC_A$ and $\beta = C_B/C_A$.

For high conversions ψ, the Mayo–Lewis equation can be written in an integral form as follows [1,3]:

$$\log([a]|_t/[a]_{t=0}) = \frac{r_A}{1-r_A}\log\left(\frac{[a]}{[b]}\right)\Big|_{t=0} \times \left(\frac{[b]}{[a]}\right)\Big|_t - \frac{1-r_A r_B}{(1-r_A)(1-r_B)}\log\frac{(r_B-1)\left(\frac{[b]}{[a]}\right)\Big|_t - r_A + 1}{(r_B-1)\left(\frac{[b]}{[a]}\right)\Big|_{t=0} - r_A + 1} . \qquad (6)$$

In the derivation of Eqn. (6) it was assumed that r_A = const. and r_B = const. Bearing in mind that $[a]/[b] = F(t)$, one may conclude that the composition of the copolymer varies with increasing ψ and that in the general case ($r_A \neq r_B$) inhomogeneity of composition appears in the specimen due to the variation of [a]/[b] in the copolymerisation process.

When data are available for the composition of the copolymer and the substrate at fixed ψ, it is possible to determine the copolymerisation constants either from Eqns. (4) and (5) for $\psi < 0.05$ or from Eqn. (6) for $\psi > 0.1$. However, the experimenter is frequently faced with a different problem—it is necessary to obtain information about inhomogeneity of composition for various ψ_t from known values of $[a]_t$, $[b]_t$, $[A]_t$, $[B]_t$, r_A and r_B. This problem has been solved in the most general form by Skeist [20].

We introduce the notation

$$f_A = \frac{[a]}{[a]+[b]}, \quad f_B = \frac{[b]}{[a]+[b]},$$
$$F_A = \frac{[A]}{[A]+[B]}, \quad F_B = \frac{[B]}{[A]+[B]} .$$

From the condition of the constancy of the total content of the monomeric units A in the substrate and the copolymer during copolymerisation, it follows that

$$f_A\{[a]+[b]\} + F_A\{d[a]+d[b]\} = \{[a]+d[a]+[b]+d[b]\}(f_A + df_A) \qquad (7)$$

and after integration

$$\log\frac{[a]+[b]}{[a]|_{t=0}+[b]|_{t=0}} = \int_{f_A|_{t=0}}^{f_A} \frac{df_A}{F_A - f_A} , \qquad (8)$$

where

$$f_A|_{t=0} = \frac{[a]|_{t=0}}{[a]|_{t=0} + [b]|_{t=0}} .$$

F_A can be determined from known values of f_A, r_A, and r_B by Eqn. (4) and then the composition and the weight fractions of the individual copolymer fractions can be found by Eqn. (8).[21]

b. "Unusual" systems. In his latest review[22] Mayo notes that one should not expect Eqns. (4)–(6) to apply to all copolymerising systems. In the literature there are no clearly formulated criteria of the applicability of the Mayo–Lewis equations to the system under consideration, although this process is frequently of decisive importance in the study of copolymerisation. At the same time a knowledge of the variation of the average composition of the copolymer with $([a]/[b])|_{t=0}$ is as a rule insufficient to determine unambiguously whether or not the system obeys Eqns. (4)–(6), because (1) there is a considerable relative indeterminacy in the positions of the points in [A]/[B]–[a]/[b] or dC_A/dC_B–C_A/C_B diagrams, since the accuracy in the determination of $\alpha_A \leq 1\%$, while

$$0 \leq dC_A/(dC_A + dC_B) \leq 1$$

and $0 \leq \alpha_A \leq 1$, and (2) even in the simplest cases of copolymerisation two parameters (r_A and r_B) are unknown and, when account is taken of the experimental error, the positions of the experimental points in the dC_A/dC_B–C_A/C_B diagram can be described by several combinations of r_A and r_B.[23–25]

In order to assess the characteristic features of the copolymerisation process, we believe it more correct to investigate the variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ [Eqn. (5)] for different substrate compositions and varying ψ rather than analyse [A]/[B] – [a]/[b] diagrams with a subsequent attempt to describe the copolymerisation process with the aid of combinations of r_A and r_B. For "classical" systems, the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ is linear, the intercept on the ordinate axis being $-r_A$ and the slope $(M_A/M_B)r_B$. The non-linearity of the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ under the condition $[A]/[B] = ([A]/[B])(t)$ $([a]/[b])|_{t=0} = \text{const.}$ is evidence that the relative reactivity of the co-monomers varies with ψ, while the non-linearity of this relation for different $([a]/[b])|_{t=0}$ indicates that the reactivity of the co-monomers varies with the composition of the substrate.

Fig. 1 shows the variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ for the "unusual" system acrylamide (Aa)–maleic acid (Ma),[26] the non-linearity of the relation between $\beta(M_A/M_B - 1/\gamma)$ and β^2/γ for the system Aa–Ma being due to changes in ψ and $([a]/[b])|_{t=0}$.

The inapplicability of the Mayo–Lewis equations to the system may be due to the failure of even only one of the six conditions formulated above in the derivation of Eqns. (4)–(6). Conditions (2), (4), and (6) are particularly important; for some systems, the fulfilment of condition (5) is not obligatory[27], and condition (3) is fulfilled automatically in the synthesis of high polymers[1,3,5].

In the general case of copolymerisation

$$r_A = r_A\{([a]/[b])|_{t=0},\ t\}$$

and $r_B = r_B\{([a]/[b])|_{t=0},\ t\}$ and one cannot expect that Eqns. (4)–(6) would then apply. A number of possible reasons for the departure of the polymerisation process from the Mayo–Lewis rule have been given in the literature.

1. The variation of the reactivity of the copolymers with the nature of the units preceding the terminal unit[28–31]. We may recall that, since "experimental errors are frequently associated with discrepancies of similar order of magnitude, a fairly marked effect of the penultimate unit has been established only in systems readily susceptible to analysis and usually for only one of the two types of radical considered".[22]

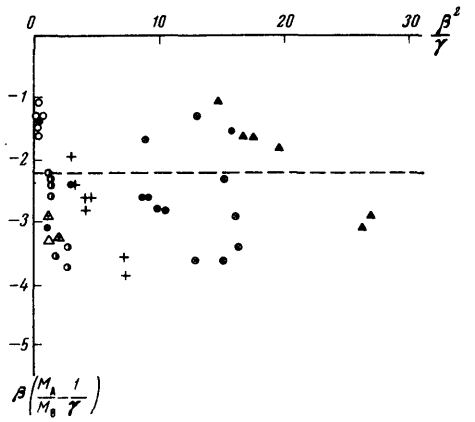

Figure 1. Variation of $\beta(M_A/M_B - 1/\gamma)$ with β^2/γ for the system acrylamide (Aa)–maleic acid (Ma). Copolymerisation in 5% aqueous solution at 70°C; the experimental points correspond to different Ψ and $([a]/[b])|_{t=0}$.

2. The appearance of phase heterogeneity in the system (precipitation of the copolymer, copolymerisation in emulsions and suspensions)[2,32,33].

3. The occurrence of a depolymerisation process in the system[34–38].

4. The occurrence in the system of chain-transfer reactions accompanied by chain rupture[39–41].

5. The dependence of the relative reactivity of co-monomers with ionogenic groups on the ionic strength of the solution[19,42–46]. This is in fact what happens in the system acrylamide–maleic acid; this system will be examined in detail below as a very clear example of "anomalous" copolymerisation.

III. INTEGRAL AND DIFFERENTIAL CURVES FOR DISTRIBUTION WITH RESPECT TO COMPOSITION

Important information about the copolymerisation process can be obtained from the analysis of integral and differential curves for distribution with respect to composition (ICDC and DCDC) when ψ and $([a]/[b])|_{t=0}$ are varied. The role of ICDC and DCDC increases markedly in the analysis of "unusual" systems where, apart from a quantitative description of inhomogeneity of composition, it is necessary to assess the causes of the "anomaly". In view of the importance of the problem and insufficient information about it in the literature[3], we shall consider in detail the method of plotting experimental and theoretical ICDC and DCDC. Here and henceforth n will be regarded as fairly large and therefore in the calculation of theoretical ICDC only the contribution due to conversion inhomogeneity of composition will be taken into account (neglecting

the instantaneous inhomogeneity). DCDC may be constructed on the basis of Eqn. (8) and, by evaluating the corresponding integral in an explicit form (as is done by Meyer and Lowry[47]) or by graphical interpolation, molar DCDC may be obtained. As an example, Fig. 2 presents the DCDC for a number of model systems (the calculation was performed by Izyumnikov and Vyrskii[48]). It is interesting to note that the DCDC is concave upwards for the case $r_A < 0.5$ (r_B can have any value) or $r_A < 0.5$ (r_A can have any value), but if $r_A > 0.5$ and $r_B > 0.5$, then the DCDC passes through the origin of coordinates[21,50]. Fig. 2 shows that the difference in the DCDC for two models, "terminal" and "preterminal", is fairly considerable and therefore by plotting the experimental DCDC one can show which model is correct.

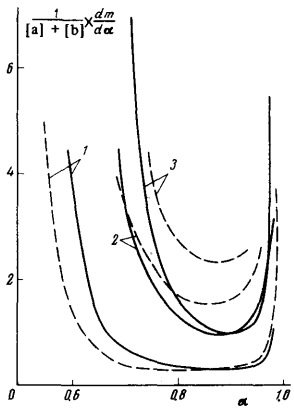

Figure 2. Differential distribution curves with respect to composition for "terminal" (dashed curves) and "preterminal" (continuous curves) models:
1) styrene–maleic anhydride; $r_A = 0.023$ and $r_B = 0.29$,[49] and also $r_A = 0.17$, $r'_A = 0.063$; and $r_B = r'_B = 0$;[48] *2*) styrene–citraconic anhydride; $r_A = 0.135$ and $r_B = 0.015$, and also $r_A = 0.07$, $r'_A = 0.25$, and $r_B = r'_B = 0.015$;[48] *3*) styrene–fumaronitrile; $r_A = 0.2$ and $r_B = 0$,[49] and also $r_A = 0.072$, $r'_A = 1.0$, and $r_B = r'_B = 0$.[48]

In order to obtain weight distribution functions with respect to composition, it is convenient to employ Eqn. (5), and, by analogy with the foregoing, to plot the DCDC. Frequently the following procedure for the plotting of ICDC and DCDC is the most convenient (one of the advantages is that initially the ICDC is plotted and then the DCDC is obtained, whereas the reverse process, the derivation of the ICDC from the DCDC, is more complex). Suppose that in the general case the equation for copolymerisation of an "unusual" system is of the form

$$dC_B = f_1(C_A|_{t=0},\ C_B|_{t=0},\ dC_A, r_A, r_B, r'_A, r'_B, r''_A, r''_B, \ldots) \qquad (9)$$

or in terms of molar concentrations

$$[B] = f_2([a]|_{t=0},\ [b]|_{t=0},\ [A],\ r_A, r_B, r'_A, r'_B, r''_A, r''_B, \ldots). \qquad (10)$$

By specifying definite values of dC_A or [b], dC_B or [B] are calculated from Eqns. (9) and (10) and then the average composition of the copolymer and the weight fraction ($dC_A + dC_B$) or the number of moles of the polymerisation increment are evaluated. After arranging the fractions in an ascending order of $\left(\frac{dC_A}{dC_A + dC_B}\right)\Big|_{\Psi - d\Psi}^{\Psi}$ or $\left(\frac{[A]}{[A]+[B]}\right)\Big|_{\Psi_1 - d\Psi_1}^{\Psi_1}$ we introduce the integral weight fraction

$$y_i = \sum_{k=1}^{i} (dC_A + dC_B)_k / (C_A + C_B)|_{t=0}$$

or

$$y'_i = \sum_{k=1}^{i} d([a] + d[b])_k / ([a] + [b])|_{t=0},$$

and $y_p = 1$ and $y'_{p'} = 1$ (p and p' are the numbers of fractions). Then the ICDC are plotted in terms of the coordinates

$$y_i - \left(\frac{dC_A}{dC_A + dC_B}\right)_i \text{ or } y'_i - \left(\frac{[A]}{[A]+[B]}\right).$$

Adequate precision in the plotting of ICDC is achieved when

$$\frac{(dC_A + dC_B)_k}{(C_A + C_B)|_{\psi=0}} \leqslant 0.001$$

with $\Psi \leqslant 0.8$, but, when the differences between r_A and r_B are not too great, the required precision in the construction of the ICDC is attained also under the condition

$$\frac{(dC_A + dC_B)_k}{(C_A + C_B)|_{\psi=0}} \leqslant 0.01.$$

Figs. 2 and 4*b* present a number of ICDC for a "classical" system corresponding to several values of Ψ, r_A, and r_B, the curves having been plotted according to the scheme described above.

Experimental ICDC can be plotted by two methods. In the first case the ICDC are obtained directly from the analysis of the copolymerisation kinetics and in the second case the required data are obtained from the analysis of the composition of the fractions. In the first variant the C_A–t and C_B–t curves are divided into 30–50 sections and the integral weight fraction and the composition of the copolymers are calculated for each section[50,51]. Figs. 3 and 4 present experimental kinetic curves and distribution curves with respect to composition constructed from these data.

In the plotting of the ICDC on the basis of fractionation data, it is desirable to have about 20 and more fractions. The fractions are arranged in terms of the ascending content of one of the components, their integral weight fractions are evaluated, and the ICDC and DCDC are plotted[26,52–55]. Experimental ICDC and DCDC obtained for the copolymers of methyl methacrylate and methacrylic acid for low values of Ψ have been plotted[56–59]; in some cases an ionising solvent—dimethylformamide—was added to the system to alter the activity of the acid units.

In the fractionation of copolymers it is very important to choose correctly the solvent–precipitant system, since in the general case the fractionation process takes place both with respect to molecular weight and composition[52–55,60]. In some cases the use of two- and even three-component solvents as precipitants proved to be the most effective[52,57]. The main theoretical principles of copolymer fractionation have been developed by Fuchs, Litmanovich, Kudryavtseva, Topchiev, and Shtern[53–55,61]. According to Kudryavtseva and Litmanovich[61], the volume

fractions of macromolecules with a degree of polymerisation n and a composition $\alpha = [A]/([A] + [B])$ in solution $(v_{n,\alpha})$ and in the precipitate $(v'_{n,\alpha})$ are related as follows:

$$\frac{v'_{n,\alpha}}{v_{n,\alpha}} = \exp[n(\sigma - \lambda\alpha)] \qquad (11)$$

where σ and λ are constants which depend on the energy and entropy parameters of the interaction in the system polymer–solvent–precipitant.

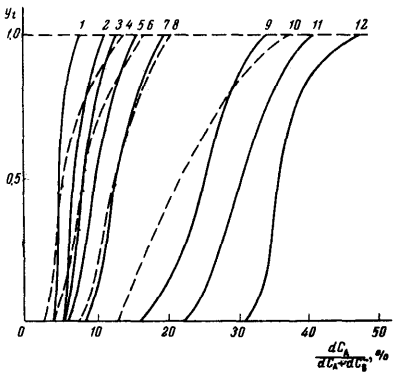

Figure 3. Integral distribution curves with respect to composition[26]. Substrate composition: acrylamide–sodium maleate: *1*) 4:1, $\Psi = 0.44$; *4*) 4:1, $\Psi = 0.82$; acrylamide–maleic acid: *2*) 9:1, $\Psi = 0.59$; *3*) 4:1, $\Psi = 0.74$; *5*) 3:1, $\Psi = 0.40$; *6*) 4:1, $\Psi = 0.85$; *7*) 3:2, $\Psi = 0.36$; *8*) 3:2, $\Psi = 0.71$; *9*) 1:1, $\Psi = 0.35$; *10*) 1:1, $\Psi = 0.43$; *11*) 2:3, $\Psi = 0.34$; *12*) 3:7, $\Psi = 0.28$; Ψ = conversion with respect to acrylamide.

Using Eqn. (11), it is possible to obtain the distribution functions with respect to composition and molecular weight for the kth fraction:

$$w_{n,\alpha}^{(k)} = w'^{(k-1)}_{n,\alpha} \frac{1}{1+P} \qquad (12)$$

$$w_n^{(k)} = \int_0^1 w_{n,\alpha}^{(k)} d\alpha = \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P} \qquad (13)$$

$$w_\alpha^{(k)} = \int_0^\infty w_{n,\alpha}^{(k)} dn = \int_0^\infty w'^{(k-1)}_{n,\alpha} \frac{dn}{1+P} \qquad (14)$$

$$P = \frac{1}{R_k} \exp[-n(\sigma_k + \lambda_k\alpha)]$$

Here $w'^{(k-1)}_{n,\alpha}$ is the distribution function with respect to n and α of the copolymer remaining in solution after the isolation of the $(k-1)$th fraction.

The parameters σ_k, λ_k, and R_k are found from the system of equations

$$\left.\begin{aligned} w^{(k)} &= \int_0^\infty w_n^{(k)} dn = \int_0^\infty dn \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P}, \\ \bar{n}_B^{(k)} &= \frac{1}{w^{(k)}} \int_0^\infty n dn \int_0^1 w'^{(k-1)}_{n,\alpha} \frac{d\alpha}{1+P}, \\ \bar{\alpha}^{(k)} &= \frac{1}{w^{(k)}} \int_0^1 \alpha d\alpha \int_0^\infty w'^{(k-1)}_{n,\alpha} \frac{dn}{1+P}. \end{aligned}\right\} \qquad (15)$$

Here $w^{(k)}$, $\bar{n}_B^{(k)}$, and $\bar{\alpha}^{(k)}$ are the weight, the weight-average degree of polymerisation, and the average composition of the kth fraction, all of which can be determined experimentally. Thus, knowing the distribution functions with respect to n and α in the initial specimen, it is possible to evaluate the distribution functions with respect to n and α for the fractions by determining $w^{(k)}$, $\bar{n}_B^{(k)}$, and $\bar{\alpha}^{(k)}$. Assuming that the distributions with respect to n and α in the initial specimen are independent, i.e.

$$w_{n,\alpha}^0 = w_n^0 \; w_\alpha^0 \qquad (16)$$

and that $r_A = 0.52$, $r_B = 0.46$, $\bar{n} = 10^3$, and $\Psi = 1$, Kudryavtseva and Litmanovich[61] estimated the possibility of consecutive, cross, and step-wise fractionation of copolymers[62]. The specimen was divided mathematically into 16 fractions according to the following scheme: initially four fractions of identical weight were obtained (*a*, *b*, *c*, *d*) and then each was in turn subdivided into four fractions of equal weight. Assuming that $R_k = 10^{-3}$ and $\lambda_k = 0.02$, $w_n^{(k)}$ and $w_\alpha^{(k)}$ were calculated on an M-20 computer,

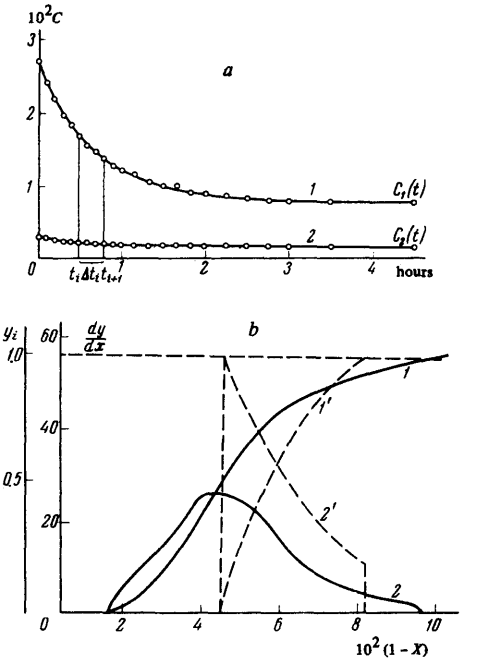

Figure 4. *a*) Curves representing the consumption of the co-monomers in 3% aqueous solution of acrylamide (curve *1*) and maleic acid (curve *2*) (9:1) at 70°C; integral (curve *1*) and differential (curve *2*) curves describing inhomogeneity of composition for $\Psi = 0.67$; *1'*) and *2*) calculated curves obtained by Skeist's method for $r_A = 2.2$ and $r_B = 0$; x = weight concentration of acrylamide in the copolymer.

assuming that Eqn. (16) applies. Fig. 5 presents the calculated distribution curves with respect to composition for all 16 fractions. It is interesting to note the overlapping of the DCDC and the at first sight paradoxical finding that the inhomogeneity with respect to composition in certain fractions (*3d*, *4a*, *4b*, *4c*, *4d*) is greater than in the initial specimen. Fig. 6 shows the differential distributions with respect to composition for two cases of fractionation. On the basis of these data, Litmanovich and Kudryavtseva conclude that cross fractionation is preferred to consecutive and stepwise fractionation.

With increasing differences in the physicochemical parameters (polarity, chemical composition, microstructure, etc.) of the homopolymeric components, the efficiency of fractionation increases. In the case of the random copolymers of methyl methacrylate and methacrylic acid, in which there is a marked difference between the properties of the homopolymeric components, good results are obtained also by consecutive fractionation[56-59]. With increasing number of fractions and stages in stepwise fractionation, the efficiency of fractionation also increases[62].

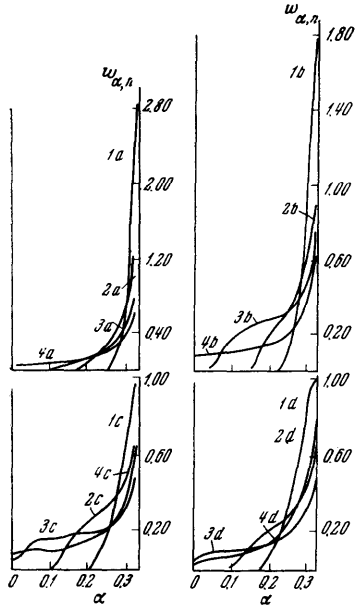

Figure 5. Inhomogeneity of the copolymer fractions with respect to composition.

Fig. 3 shows the ICDC for the acrylamide–maleic acid copolymers. The number of fractions analysed for each specimen was not less than 38.[26] Here sufficiently effective fractionation was attained partially also because the conformational and thermodynamic stability of the macromolecules in solution depends significantly on the concentration of the inorganic acid groups in the macromolecule (we emphasise that a polyelectrolyte system was fractionated). In this connection it is of interest to estimate the effectiveness of fractionation with respect to composition as a function of the ionic strength of the solution, but the amount of experimental data of this kind is much too small for final conclusions.

It has already been stated that the copolymerisation of "unusual" systems can be most conveniently analysed with the aid of ICDC or DCDC. We shall consider in somewhat greater detail concrete "anomalous" systems. When the relative reactivity is influenced by the nature of one, two, and three terminal units of the growing chain, it is necessary to introduce respectively two, four, and eight probabilities of the addition of units A and B. It has been shown[63] that the study of the average composition of copolymers does not show unambiguously whether the penultimate units have an effect or not. At the same time, as already mentioned by Vyrskii and Izyunikov[48], it has been shown that ICDC and DCDC are fairly sensitive characteristics which can be used to decide which model (terminal or preterminal) is to be preferred.

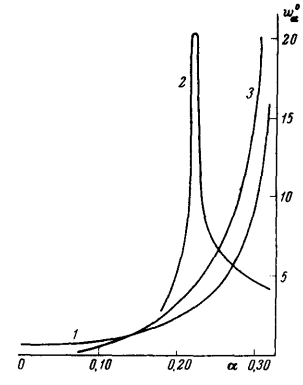

Figure 6. Differential distribution curves with respect to composition for the initial copolymer: specified curve (curve *1*) and curve plotted on the basis of branched (curve *2*) and cross (curve *3*) fractionation.

Fig. 7 presents the ICDC for the copolymer of acrylamide and maleic acid and the total inconsistency between the experimental and theoretical ICDC, going far beyond the possible experimental errors, is evidence that the Mayo–Lewis equation does not apply to this system[64].

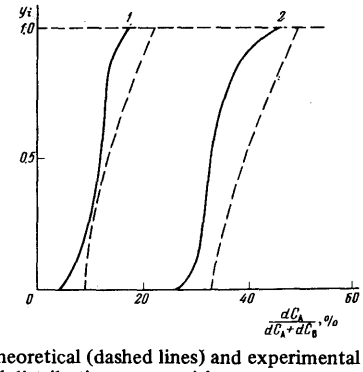

Figure 7. Theoretical (dashed lines) and experimental (continuous lines) integral distribution curves with respect to composition. Substrate composition for the acrylamide–maleic acid system: *1*) 4:1, $\Psi_A = 0.56$; *2*) 2:3, $\Psi_A = 0.04$; Ψ_A = conversion with respect to acrylamide.

This can be explained by the non-isoionic nature of the copolymerisation process, since the ionic strength is different for different substrate compositions and furthermore the effective dissociation constant of maleic acid can vary in the copolymerisation process[65-67]. To illustrate the effect of the ionic strength of the solution on the nature of the ICDC Figs. 8 and 9 present the curves for the system at different pH and concentrations of co-monomers. These

data confirm the conclusion that the effective dissociation constant of maleic acid influences the relative reactivity in its addition to the macroradical with a terminal acrylamide unit. As in the studies of a number of investigators[26,48,64], when an "anomaly" appears in a copolymerising system, a relative increase in inhomogeneity of composition compared with "classical" systems is to be expected. Considerable spreading of the ICDC and DCDC may be expected also when account is taken of instantaneous inhomogeneity of composition whose contribution to the total inhomogeneity should increase as the molecular weight of the copolymers falls[53]. In principle, instantaneous inhomogeneity of composition may be estimated by analysing the ICDC for fixed values of [a]/[b] and Ψ by varying n (in the simplest case by varying the concentration of the initiator in the copolymerising system), but an approach of this kind requires a degree of precision in the plotting of the ICDC higher than can be attained at the present time.

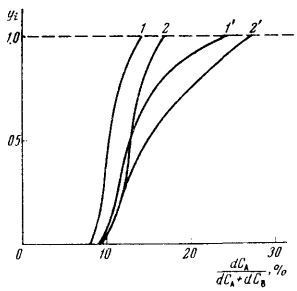

Figure 8. Integral distribution curves with respect to composition in the presence and absence of added phosphoric acid[26]. Substrate composition for the acrylamide–maleic acid system: *1*) 7:3, $\Psi = 0.60$; *1'*) 7:3, $\Psi = 0.56$; *2*) 1:1, $\Psi = 0.50$; *2'*) 1:1, $\Psi = 0.39$; curves *1* and *2* were obtained with added phosphoric acid at pH 1.4 and curves *1'* and *2'* were obtained without added phosphoric acid [*1'*) pH 1.64; *2'*) pH 1.50].

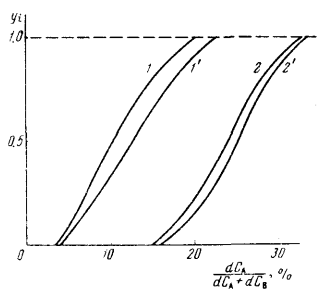

Figure 9. Integral distribution curves with respect to composition for 5% solutions at pH 1.58 (curves *1* and *1'*) and 10% solutions at pH 1.42 (curves *2* and *2'*)[26]; Composition of substrate-acrylamide: maleic acid = 65:35; polarographic data: *1*) $\Psi = 0.60$; *2*) $\Psi = 0.33$; fractionation data: *1'*) $\Psi = 0.71$; *2'*) $\Psi = 0.71$.

The instantaneous inhomogeneity can also be estimated from the analysis of the structure of the macromolecules obtained by the "dose" method[68–71].

IV. ANALYSIS OF THE CHEMICAL STRUCTURE OF COPOLYMERS

Using the principle of reversibility[2], it can be shown that the necessary information about the process can be obtained not only from a comparison of the copolymerisation parameters but also from the analysis of the "formed" macromolecules. The scope of the study of the chemical structure of copolymers is analysed in Kantov's review[72]. We are interested in problems concerning the relation between instantaneous inhomogeneity of composition and the chemical structure of the macromolecule. The chemical structure may be regarded as known if the probabilities of different sequences of monomeric units A and B have been determined, without taking into account the differences in the stereochemical configurations within the sequences. According to the literature[73,74],

$$w_{AA} = \frac{r_A [a]}{r_A [a] + [b]} \text{ and } w_{BB} = \frac{r_B [b]}{r_B [b] + [a]},$$

whence the probability of the formation of blocks of n units of monomer A is

$$P_A(n) = w_{AA}^{n-1}(1 - w_{AA})$$

and the fraction of the units A in blocks consisting of n units is

$$F_A(n) = \frac{nP_1(n)}{\sum_{n=1}^{\infty} nP_1(n)} = \frac{nw_{AA}^{(n-1)}}{\sum_{n=1}^{\infty} nw_{AA}^{(n-1)}}. \quad (17)$$

After simple transformation, we have

$$F_A(n) = n(1 - w_{AA})^2 w_{AA}^{(n-1)}. \quad (18)$$

Similarly,

$$F_B(n) = n(1 - w_{BB})^2 w_{BB}^{(n-1)}, \quad (19)$$

and from the normalisation condition we obtain

$$\sum_{n=1}^{\infty} F_A(n) = \sum_{n=1}^{\infty} F_B(n) = 1.$$

By estimating the probabilities of the formation of different triads, it can be shown that

$$\left.\begin{aligned} &F_{AAA} = w_{AA}^2;\ F_{BBB} = w_{BB}^2;\ F_{AAB} + F_{BAB} = 2w_{AA}(1 - w_{AA}),\\ &F_{BBA} + F_{AAB} = 2w_{BB}(1 - w_{BB});\ F_{ABA} = (1 - w_{BB})^2,\\ &F_{BAB} = (1 - w_{AA})^2;\ F_{AAA} + F_{BAA} + F_{AAB} + F_{BAB} = 1. \end{aligned}\right\} \quad (20)$$

Similarly it is possible to calculate the probability of more complex combinations of units A and B.

In order to obtain direct information about the chemical structure of the macromolecules of the copolymers, it is possible to use a number of spectroscopic or radiospectroscopic (nuclear magnetic resonance) techniques and also chemical methods—see the reviews in the literature[75–77]. However, the application of even the best of these methods, for example nuclear magnetic resonance, does not as yet ensure the necessary accuracy for reliable estimates of instantaneous and conversion inhomogeneity of composition[78–80].

There are fundamental reasons why methods such as X-ray diffraction structure analysis, differential thermal analysis[81], and electrical and mechanical methods for the investigation of polymers in the solid state[82] are unsuitable for the determination of inhomogeneity of composition. The point is that these methods are "sensitive" to the behaviour of relatively large sections of the chains; therefore they can, for example, distinguish block or graft copolymers from random copolymers (if the blocks or

branches are sufficiently large), but, as regards random polymers, they can "detect" to some degree only the *average* composition.

This applies equally to optical methods, which can determine any one characteristic—for example optical density[83], refractive index, etc.

The situation changes significantly, however, if measurements of this kind can be combined with the second ("fractionating" [2]) parameter and (or) one of the components of the copolymers is "masked". The "masking" principle was first applied in the light scattering method. The principal theoretical postulates and the available experimental results obtained by this method are described in the reviews of Benoit[84] and Eskin[85].

It has been shown[86-88] that the molecular weight of the copolymer M_{app} obtained by the usual extrapolations is a function of the true weight-average molecular weight $\overline{M}_B$ and the statistical parameters P and Q, which characterise the polydispersity and the inhomogeneity of the copolymeric specimens with respect to composition:

$$M_{app} = \overline{M}_B + \frac{(2\nu_A - \nu_B)}{\nu} P + \left(\frac{\nu_A - \nu_B}{\nu}\right)^2 Q. \qquad (21)$$

Here

$$P = \sum_i \sum_j \gamma_{ij} M_{ij} \delta x_{ij} = \frac{1}{2}[(1-\bar{x})(\overline{M}_B - \overline{M}_B^A) - \bar{x}(\overline{M}_B - \overline{M}_B^B)], \qquad (22)$$

$$Q = \sum_i \sum_j \gamma_{ij} M_{ij} \delta x_{ij}^2 = \bar{x}(1-\bar{x})(\overline{M}_B^A + \overline{M}_B^B - \overline{M}_B), \qquad (23)$$

where γ_{ij} is the relative fraction of macromolecules with $\delta x_{ij} = x_{ij} - \bar{x}$, $\overline{M}_B^A$ and $\overline{M}_B^B$ are the true weight-average molecular weights of the hypothetical sequences or blocks (in block copolymers) of components A and B the refractive increments for which are respectively ν_A and ν_B, and $\bar{x}$ is the weight-average content of component A in the copolymer.

The summation in Eqns. (22) and (23) is carried out with respect to two parameters, taking into account the fact that in the general case differences in composition are assumed within *ensembles* of macromolecules with the same molecular weight and differences in molecular weight within macromolecules with the same chemical composition. It can be shown that

$$-\bar{x}\overline{M}_B \leqslant P \leqslant (1-\bar{x})\overline{M}_B,$$
$$0 \leqslant Q \leqslant [1-\bar{x}(1-\bar{x})]\overline{M}_B.$$

Of course, P and Q have maximum values for a mixture of homopolymers. The parameter P characterises the change in the composition of the copolymeric system with the molecular weight and Q characterises the dispersion of the specimen with respect to composition and depends on the molecular weight distribution within the specimen.

Theoretical relations (21)–(23) have been tested[89-95] on a series of model systems (statistical, block copolymers, graft copolymers, mixtures of homopolymers) and it has been established that the $\overline{M}_B$, $\overline{M}_B^A$, and $\overline{M}_B^B$ data obtained by light scattering measurements are quite reliable and theoretically justified. Fairly convincing data are obtained for block copolymers by the light scattering method and from determinations based on root mean square radii of inertia of the macromolecule and components A and B.[96] At the same time details and even merely true information about the inhomogeneity of copolymers with respect to composition cannot, be obtained, in principle, for all copolymeric systems and the reliability of such data is in many cases low.

There are several reasons for this: (1) the light scattering method yields reliable results for systems with $\overline{M}_B > 10^4$; (2) in order to obtain P and Q data, it is necessary to have at least three solvents with significantly differing (by not less than 0.05) refractive indices; the solvents must all dissolve the homopolymeric components; this essential condition significantly complicates the analysis of copolymers and makes it almost impossible to obtain (by the light scattering method) data on inhomogeneity of composition in systems where one of the components is hydrophobic and the other hydrophilic; (3) the difference in the refractive indices of the homopolymeric components must be more than 0.05; (4) the parameters P and Q depend on the molecular weight distribution within the specimens and therefore are not unambiguous characteristic of the inhomogeneity; (5) the P and Q data can be obtained only for copolymers of definite composition ([A]/[B] < 10 when [A] > [B] and [A]/[B] > 0.1 when [A] < [B]); (6) the accuracy of the determination of P and Q is inadequate for many systems and this is mainly responsible for the anomalously high value of Q in certain systems. Thus, according to the data of Baranovskaya et al.[97] for statistical styrene–methyl methacrylate copolymers ($r_A = 0.46$ and $r_B = 0.52$), we have $Q/Q_{max} \simeq 0.4$ for [a]/[b] $\simeq \frac{1}{3}\Psi = 0.7$, which is more than ten times greater than the values of Q/Q_{max} calculated by Skeist's method. It was assumed that $Q_{max} = [1 - X(1-X)]\overline{M}_B$, i.e. the extremal value characteristic of a mixture of homopolymers. Such marked inconsistency between the calculated and experimental values of Q/Q_{max} cannot be attributed to instantaneous inhomogeneity of composition, since the system investigated by the authors had a fairly high molecular weight. In somewhat later studies for a similar copolymeric styrene–butyl methacrylate system Eskin et al.[98] obtained $Q/Q_{max} \simeq 0.1$, which is also higher than the calculated values of Q/Q_{max} but in this case the calculated and experimental quantities are of the same order of magnitude. The application of the light scattering method in the analysis of azeotropic styrene–methyl methacrylate copolymers[99] showed that the sensitivity of the method is insufficient to assess the conversion inhomogeneity of composition when the inhomogeneity is low. The authors' conclusion concerning the "anomaly" of one of the ten specimens were not confirmed by data derived by other methods.

In the authors' view the data on inhomogeneity of composition obtained by studying light scattering in copolymer solutions in different solvents must be compared with data obtained by direct estimates of the inhomogeneity; in particular, such combined estimates are essential in the study of statistical copolymers.

We have already emphasised that in this case $\overline{M}_w^A$ and $\overline{M}_w^B$ are *fictitious* quantities which correspond to *hypothetical* sequences of A and B units in each molecule of the *ensemble* investigated. However, even the *optical* properties of this "equivalent" copolymer can differ from those of the statistical copolymer; the interaction of adjacent units of different types may influence the refractive index increments, the average root mean square fluctuation of the refractive index may alter, etc.

It is far from being our desire to "invalidate" the light-scattering method as applied to the analysis of inhomogeneity of composition; we merely wish to stress that, apart from the purely experimental difficulties enumerated above, the method also has certain fundamental limitations, which have not yet been overcome for statistical copolymers.

The scope of the method of sedimentation in a density gradient for the estimate of inhomogeneity of composition is discussed in the review of Hermans and Ende[100]. Un-

fortunately the authors do not consider the problem of the effect of selective solvation on the spreading and displacement of the constant-density curve[2], although this is one of the urgent problems in the study of copolymeric systems[2,4]. Using the sedimentation data, Hermans and Ende[101] made an approximate estimate of inhomogeneity of molecular weight and composition. They chose for investigation the statistical copolymer of styrene and iodostyrene. The weight content of iodine in the fractions varied from 20 to 27% (the average content of iodine in the specimen was 24.15%), i.e. the specimens investigated showed appreciable inhomogeneity of composition. A significant difference in the apparent densities of the homopolymeric components favoured an effective estimate of inhomogeneity of composition. Equilibrium sedimentation in a density gradient was studied at 12°C, i.e. virtually at the θ-point[4]; as a precaution, the concentration effect was excluded by extrapolation to $C = 0$. It was shown that the method employed makes it possible to estimate the width of the distribution with respect to composition with an accuracy of about 20%.

It is noteworthy that one of the most difficult problems in the study of the sedimentation equilibria of copolymers is the separation of the effective broadening of the constant-density line due to inhomogeneity of composition and of molecular weight.

In Baldwin and Schooter's method[102] account is taken of the different inertia in the rearrangement of the constant-density lines in a variable acceleration field for macromolecules with different chemical compositions and different molecular weights. It should be borne in mind that in all cases of analysis of sedimentation data it is extremely difficult to convert them into functions which give a quantitative description of inhomogeneity of composition. As a rule, it is necessary to resort to not altogether justifiable assumptions and much preliminary information about the system is required[2]. Furthermore, sedimentation analysis itself cannot be applied to all systems—it is essential to have adequate differences between the densities and refractive indices of the dissolved species and solvent molecules.

We believe that significant progress may be expected in the study of equilibrium sedimentation for two types of system.

1. A system which is almost homogeneous with respect to molecular weight but is significantly polydisperse with respect to composition. This case is realised most simply by controlled polymerisation-like reactions involving the functional groups of the macromolecules[71,103,104]. With increase of the differences in the densities of the homopolymeric components, analysis of inhomogeneity of composition is facilitated.

2. A system which is almost homogeneous with respect to composition (for example in the case where $r_A = r_B = 0$ strict alternation of A and B units may be expected in the macromolecules regardless of the composition of the substrate when $n \gg 1$), but the fractions differ in their molecular weight. Then the usual[2] quantitative estimate of polydispersity with respect to molecular weight is possible for copolymeric systems where the macromolecules are almost homogeneous with respect to chemical composition.

A combination of the "masking" and high-speed sedimentation methods, which permits in principle the determination of the ICDC and DCDC, shows promise for the description of inhomogeneity of composition. Additional possibilities in the estimation of polydispersity with respect to composition and with respect to molecular weight may be expected when sedimentation and polarographic analyses are combined[106]. In this case it is possible in principle to derive information about the ICDC and the molecular weight distribution in the copolymerising system for different values of ψ.

Klenin et al.[107] showed that in certain specific cases the inhomogeneity of copolymers with respect to composition can be estimated with the aid of a polarisation diffusiometer. The scope of the method has been illustrated using as an example styrene–methyl methacrylate graft copolymers. The authors note that the method is applicable to systems where the variation of the molecular weight of the fractions is related to the variation of their chemical composition. It may be noted that the estimation of inhomogeneity of composition in statistical copolymers with a large set of fractions having different compositions (in particular in the estimation of conversion inhomogeneity) involves enormous difficulties and is scarcely suitable for determinations with a polarisation diffusiometer.

V. QUANTITATIVE ESTIMATION OF THE INHOMOGENEITY OF COPOLYMERS WITH RESPECT TO COMPOSITION

The ICDC and DCDC are the most complete characteristics of the inhomogeneity of copolymers with respect to composition[2,3] and in certain cases it is possible to obtain information about the characteristic features of the copolymerisation reaction from ICDC and DCDC data; in the first place this applies to "anomalous" systems. While noting the great promise of the method involving the comparison of the ICDC, the specific difficulties in the quantitative estimates of inhomogeneity of composition from ICDC data, which are caused in the first place by the different shapes of the curves, must be emphasised. Therefore it is quite justifiable to employ for the quantitative estimate of inhomogeneity of composition, statistical characteristics which represent the ratios of various moments of the distribution with respect to composition[108]. These characteristics are similar to parameters of the Schulz type[109], which are used to describe polydispersity with respect to molecular weight.

Let us consider again a two-component (A and B) copolymeric system; there are no residual monomers. The molecular weight distribution within the specimen may be of any kind, but, in order to exclude random fluctuations with respect to composition, it is assumed that oligomer molecules are absent from the specimen. Let the specimen contain "K" fractions differing in composition and let each fraction consist of macromolecules of the same composition. If $x_1, x_2, x_3, \ldots, x_i, \ldots, x_k$ are the weight contents of component A in the fractions and $\omega_1, \omega_2, \omega_3, \ldots, \omega_i, \ldots, \omega_k$ are the weight concentrations of the fractions in the specimen ($\sum_{i=1}^{k} \omega_i = 1$), then it is possible to calculate the parameters characterising the average composition of the specimen (it is assumed that ω_i and x_i are known for all the fractions). In the general case, by analogy with q, the average molecular weights[2], it is possible to introduce, on the basis of the weight average, a "P-average" composition defined as the ratio of the distribution moments with respect to composition of orders P and $P - l$:

$$x_p = \frac{\bar{x}_p}{\bar{x}_{p-1}} = \frac{\int_0^1 x^p \omega(x)\,dx}{\int_0^1 x^{p-1}\omega(x)\,dx} \cong \frac{\sum_{i=1}^{k} x_i^p \omega_i(x)}{\sum_{i=1}^{k} x_i^{p-1}\omega_i(x)} \qquad (24)$$

and

$$\int_0^1 \omega(x)\,dx = \sum \omega_i = 1 \ .$$

Parameters of the form $f = x_p/x_q - 1$ ($f > 0$ when $P > q$), for example,

$$f_1 = \sum_{i=1}^{k} \omega_i x_i \sum_{i=1}^{k} \frac{\omega_i}{x_i} - 1 \ , \tag{25}$$

$$f_2 = \frac{\sum_{i=1}^{k} \omega_i x_i^2 \sum_{i=1}^{k} \frac{\omega_i}{x_i}}{\sum_{i=1}^{k} \omega_i x_i} - 1 \ , \tag{26}$$

etc, characterise quantitatively the inhomogeneity of composition but the use of the parameter f and its analogues for the estimation of the inhomogeneity is not possible in all cases. In the first place this is because the values of f_1, f_2, and f_3 depend significantly on $\bar{x}_p$ and furthermore the condition $f(A) = f(B)$ or $f(x) = f(1 - x)$ must hold, i.e. the parameter of inhomogeneity of composition should not depend on the nature of the components of the copolymeric system. It is reasonable to assume that the inhomogeneity is determined solely by the shape and width of the ICDC and DCDC and is independent of x_p, i.e. in the general case the following condition should hold:

$$f(x_1, x_2, x_3, \ldots x_i, \ldots x_k) = f(x_1 + x_0, x_2 + x_0, x_3 + x_0, \ldots x_i + x_0, \ldots x_k + x_0), \tag{27}$$

where $x_0 = \text{const}$.

Furthermore the required function of inhomogeneity of composition must have finite values also when $x = 0$ and $x = 1$, which is not the case for f_1 and f_2. Kantov's parameters[72] do not satisfy completely the requirements formulated [in particular the requirement defined by Eqn. (27)]. In terms of the present notation, this parameter is

$$f_3(A) = \frac{\sum_{i=1}^{k} P_i^{(+)}(A)\,\Delta\alpha_i^{(+)}\cdot(A)}{\sum_{i=1}^{k} P_i^{(+)}(A)} + \frac{\sum_{i=1}^{k} P_i^{(-)}(A)\,\Delta\alpha_i^{(-)}(A)}{\sum_{i=1}^{k} P_i^{(-)}(A)} = U^{(+)}(A) + U^{(-)}(A), \tag{28}$$

$$f_4(A) = \frac{U^{(+)}(A)}{U^{(-)}(A)} \ .$$

Here $P_i^{(+)}(A)$ is the weight content of the fractions in the specimen with $\alpha_i(A) = \bar{\alpha}_B(A) + \Delta\alpha_i(A)$ and $\bar{\alpha}_B < \alpha_i(A)$ $P_i^{(-)}$ —the weight content of the fractions in the specimen with $\Delta\alpha_i(A) = \bar{\alpha}_B(A) - \alpha_i(A) > 0$. It can be shown that the above requirements are satisfied by the parameter

$$f_5 = (\bar{x}_z - \bar{x}_B)\,x_B \tag{29}$$

where

$$\bar{x}_z = \frac{\sum_{i=1}^{k} \omega_i x_i^2}{\sum_{i=1}^{k} \omega_i x_i} \quad \text{and} \quad \bar{x}_B = \sum_{i=1}^{k} \omega_i x_i \ .$$

To illustrate the scope of the analysis of inhomogeneity of composition on the basis of ICDC and DCDC, we shall employ experimental data obtained for the system acrylamide (Aa)–maleic acid (Ma) by polarographic analysis[26]. Since maleic acid is incapable of homopolymerisation, $r_B = 0$ for this system. Analogous conclusions can be arrived at when other reasonable values of r_B in the range $0 < r_B \leq 0.05$ are used instead of $r_B = 0$. To calculate f_5, the ICDC were divided into 20–30 sections and the composition and weight fraction of each polymer fraction was calculated for each section.

To compare the relative extents of inhomogeneity of composition, it is most convenient to employ the parameter

$$y = \frac{f_5'}{f_5''} - 1 \tag{30}$$

where f_5' and f_5'' are the experimental and theoretical values of f_5 calculated for the same substrate composition.

Fig. 10 presents data on the variation of y with substrate composition. Analogous results are obtained also when other fixed values of r_A and r_B are used. Fig. 10 shows that $y > 0$ for all γ, which is evidence of the "anomalous" nature of the copolymerisation in the acrylamide–maleic acid system (for an "ideal" system $y \simeq 0$).

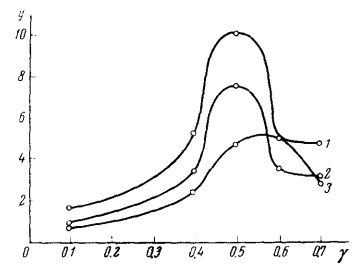

Figure 10. Variation of y with γ (γ is the weight content of maleic acid in the substrate) for certain values of r_A and r_B: *1*) $r_A = 2.2, r_B = 0$; *2*) $r_A = 1.0$, $r_B = 0$; *3*) $r_A = 3.0, r_B = 0$.

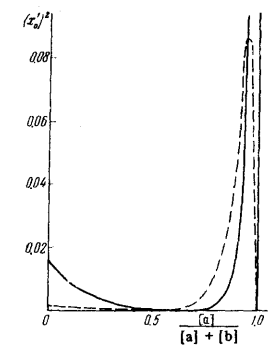

Figure 11. Variation of $(x_0')^2$ with α_A for "terminal" (dashed curve) and "preterminal" (continuous curve) models of the styrene–fumaronitrile system for $\alpha_A = 0.99$ and $(x_0')^2 = 3.7$; $(x_0')^2$ = variance with respect to composition.

This is in fact understandable—the copolymerisation of the acrylamide–maleic acid system is non-isoionic and cannot be described with the aid of fixed values of r_A and r_B, since the reactivities of the co-monomers vary during the copolymerisation process and depend on substrate composition.

In the study already quoted[48] the variance of the distribution with respect to composition σ^2 (for the number average) for the "terminal" and "preterminal" model systems (ψ small) was calculated. Fig. 11 presents the

variation (determined by Izyumnikov and Vyrskii) of $(\varkappa_0')^2 = 12\sigma^2\psi^2$ for various substrate compositions. The data show that the quantitative estimate of inhomogeneity of composition may help determine which model ("terminal" or "preterminal") gives the best description of the real copolymerisation process. We may recall that this cannot be done on the basis of data on the average composition[63].

There is no doubt about the existence of an unambiguous relation between inhomogeneity of composition and the inhomogeneity of the distribution of sequences within the copolymer macromolecule, but so far these relations have not been obtained in an analytical form. Nevertheless the study of the distribution of sequences within the macromolecule can already yield some information about the inhomogeneity of the composition of the copolymeric specimen[72]. It can be shown that the number-average $[\bar{n}(A)]$ and weight-average $[\bar{n}_B(A)]$ lengths of the real sequences of A units are related to the copolymerisation constant r_A:

$$\bar{n}(A) = 1 + r_A\frac{[A]}{[B]}, \qquad (31)$$

$$\bar{n}_B(A) = 1 + 2r_A\frac{[A]}{[B]}. \qquad (32)$$

To characterise the differential inhomogeneity of the sequences, it is convenient to introduce the parameter

$$\lambda(A) = \frac{\bar{n}_B(A)}{\bar{n}(A)} - 1 = \frac{r_A[A]}{r_A[A] + [B]}. \qquad (33)$$

After integration of the function $\lambda(A)$ over all ψ, it is possible to obtain the integral inhomogeneity of composition. It should be noted that, in view of the inadequate sensitivity of the experimental methods, the experimental value of $\lambda(A)$ cannot be compared with the theoretical value [based on Eqn. (33)].

Thus by estimating the inhomogeneity with respect to composition in the system with the aid of parameters of the type of y, it is possible to obtain definite information also about the copolymerisation process itself: namely, the greater is the deviation of y from zero the more anomalous is the system. Having established this fact, it is now possible to seek the reasons for this anomaly in accordance with the principle of "preliminary" analysis described by Frenkel'[2].

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In the extensive scientific literature on the problems of copolymerisation, there are very few papers on the analysis of the polydispersity of copolymers with respect to composition despite the fact that it is precisely by plotting the ICDC or on the basis of quantitative estimates of inhomogeneity of composition that one can arrive at direct conclusions concerning the characteristic features of the copolymerisation process itself. At the same time the widely employed data on the average composition of copolymers (for fixed values of ψ) as a rule do not allow the correct interpretation of the copolymerisation mechanism. For the assessment of the "anomalous" systems, ICDC and DCDC are just as necessary as information about the molecular weight distribution of the polymers in the analysis of the mechanism and in the estimation of the kinetic parameters of homopolymerisation[2]. In this connection it is now essential to develop studies where the section "discussion of the results" in the relevant paper involves the comparison of the experimental and theoretical ICDC for concrete copolymerisation mechanisms; at the same time studies on the quantitative estimation of inhomogeneity of composition for various substrate compositions are bound to be of interest. Experimental investigations dealing with the estimation of the contribution of instantaneous inhomogeneity of composition to the overall inhomogeneity are likewise necessary. At the present time maximum caution must be exercised in the classification of concrete copolymerising systems as "classical" or "anomalous". For example, the attempts to apply the Mayo–Lewis equations to describe "unusual" systems is known to be incorrect on *a priori* grounds.

Completely new and interesting evidence has been obtained in studies[110,111] on the copolymerisation of acrylic acid with maleic and fumaric anhydrides. According to the authors of these investigations, in order to describe the copolymerisation process, it is necessary to derive a reaction mechanism taking into account the formation of active complexes and the copolymerisation reaction itself may be classified as "unusual" ("anomalous").

The likelihood of the erroneous interpretation of the characteristic features of copolymerisation is greatly reduced if, instead of data on the average composition of copolymers, ICDC and DCDC are employed. In this sense the problem which we attempted to describe is quite similar to the *combined* kinetic and statistical analysis of homopolymerisation mechanisms[2].

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The Dependence of the Mechanism of the Hydrolysis, Trans-esterification, and Trans-etherification of α,β-Alkenyl Ethers and Esters on Their Structure

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New experimental data obtained in the study of the mechanism of the hydrolysis of ethers and esters formed by enols and the related trans-esterification and trans-etherification of these compounds are collected in the present review.
Recent studies have confirmed the early views that the hydrolysis of the ethers formed by enols passes through a stage involving hydration of the ethylene bond, have made it possible to describe this reaction scheme in considerable detail, and have shown that an analogous mechanism can be extended to the hydrolysis of the esters formed by enols, in the discussion of which, until recently, schemes involving nucleophilic substitution at the carbonyl group were used.
The large amount of data on the alkaline hydrolysis of enol acylates indicates that the mechanism of this reaction is similar to, but not identical with that of the alkaline hydrolysis of alkyl esters.

CONTENTS

1. Introduction	1009
2. Point of Fission of the bonds in hydrolysis	1010
3. Acid hydrolysis of ethers	1012
4. Acid hydrolysis of esters	1014
5. Trans-esterification and trans-etherification (vinyl exchange)	1017
6. Hydrolysis of ethers and esters catalysed by mercury salts	1018
7. Alkaline hydrolysis of esters	1019

1. INTRODUCTION

Modern theories of equilibrium and the kinetics of chemical reactions are based on the classical studies of Menshutkin, carried out in the eighteen-hundreds. The object of these studies was the formation and hydrolysis of esters. Fifty years later, Polanyi and Szabo, using ^{18}O, determined the point of fission of the bonds in the hydrolysis of esters of carboxylic acids. This work became a classical example of the use of tracers to investigate reaction mechanisms. Since that time, a large number of workers, including a number of outstanding chemists of the present time, have taken part in the study of the details of the mechanism of esterification and etherification and the hydrolysis of ethers and esters. It is therefore not surprising that the hydrolysis, trans-esterification, and formation of esters are among the processes which have been studied most fully and in greatest detail, in both preparative and theoretical aspects.

The foregoing is only partly true of ethers and esters with characteristic structure in which the ether oxygen atom is next to an ethylenic bond. These are the $\alpha\beta$-alkenyl ethers and esters, which are often also called enol ethers and enol acylates or carboxylates. Studies of the chemistry of this group of ethers and esters have been chiefly of a practical nature, and the mechanism of their transformations has been little studied. Until recently, there was very little published information on the kinetics of the hydrolysis of vinyl ethers and esters, and no direct data on the point of fission of the bonds. In the discussion of the mechanism of the hydrolysis of these compounds, the authors restricted themselves to the analogy with the well-studied processes involving the corresponding alkyl ethers and esters[1-3].

Interest in the mechanism of the transformation of $\alpha\beta$-alkenyl ethers and esters began to increase in the late nineteen-fifties, when the intensive development of the theory of polymerisation brought to the forefront the problem of the dependence of the reactivity of monomers on their structure. The study of the mechanism of hydrolysis of vinyl ethers and esters from this viewpoint has extended in the last ten years to such an extent that the main regular features have now been outlined. It can therefore be regarded an appropriate time to summarise the results. A summary on this basis is also of interest in connection with the theory of the other reactions of these compounds.

The chemical properties of $\alpha\beta$-alkenyl ethers and esters, which have been studied in detail and described in reviews and monographs[1-7], show a similarity in the behaviour of ethers and esters of this type in reactions with acidic reagents, and demonstrate the high reactivity of their ethylenic bond in electrophilic addition, which obeys Markovnikov's rule.

The activation of the double bond can be attributed to conjugation of the π-electrons with the unshared pairs of electrons of the ether oxygen atom:

$$CH_2=CH-\ddot{O}-R\,.$$

According to Wheland's calculations[8], the conjugation energy in methyl vinyl ether is 3.6 kcal mole^{-1}. In accordance with this, the signal of the β-hydrogen atoms of the vinyl group in the proton magnetic resonance (PMR) spectra of enol ethers is displaced towards higher fields compared with the signal of the hydrogen atoms of the ethylene group in simple alkenes[9], and the frequency of the out-of-plane bending vibrations of the $=CH_2$ group† in the infrared spectrum of enol ethers is lower than that for alkenes[10].

In enol acylates, the conjugation of the vinyl group with the ether oxygen should be weakened by the influence of the electron-accepting carbonyl group. The extent to which this decreases the polarisation of the ethylenic bond can be estimated from spectroscopic data (Table 1), which indicate that in alkenyl carboxylates the C=C bond is less extensively polarised than that in methyl vinyl ether, but more extensively polarised than that in propene. Thus conjugation of the ether oxygen with the ethylenic bond still plays an important part.

Table 1. Spectroscopic data characterising the polarisation of the double bond.

Compound	Chemical shift δ of the β-hydrogen atoms in the PMR spectrum	References	Frequencies of the out-of-plane bending vibrations of the CH_2 group in the infrared spectra, cm^{-1} (Ref.10)
Ethylene	5.33	14	—
Propene	4.96	14	912
Methyl vinyl ether	4.05	9	811
Vinyl acetate	4.67	12	870
Isopropenyl acetate	4.62	13	
Vinyl benzoate	4.75	13	870
Methyl vinyl ketone	6.09	14	955

Enol ethers are stable in alkaline media, but are readily hydrolysed in weakly acidic and even neutral aqueous solutions, and this distinguishes them sharply from dialkyl ethers. For example, the rate of the acid hydrolysis of ethyl vinyl ether is greater than that of diethyl ether by a factor of $10^{13.15}$[15] The increase in the rate of hydrolysis of ethers when an ethylene bond is introduced in the α-position relative to the oxygen has been attributed to hydration of the C=C group, preceding the splitting of the bonds in the ether, as shown in the scheme:

$$CH_2=CH-OR+\overset{+}{H_3O}\rightarrow CH_3CH\begin{matrix}OR\\ \diagup\\ \diagdown\\ \underset{+}{OH_2}\end{matrix}\rightarrow ROH+CH_3CH=\overset{+}{O}H\,. \qquad (1)$$

The hydrolysis of αβ-alkenyl acylates, like the hydrolysis of the esters of saturated alcohols, is catalysed by both acids and alkalis. The rates of the acid and alkaline hydrolysis of alkenyl and alkyl acylates differ by not more than two orders of magnitude. The outward similarity in the stoichiometry of the reaction, which for the hydrolysis of vinyl esters can be represented by the equation

$$CH_2=CH-OCOR+H_2O\rightarrow CH_3=CH-OH+RCOOH \qquad (2)$$

† The change in this quantity can give information on the change in the π-charge on the carbon atom[11].

together with their identical catalytic behaviour, suggest that in the hydrolysis of acylates the introduction of the ethylenic group in the α-position to the ester oxygen atom does not alter the reaction mechanism[1-3]. This justifiable assumption probably also explains why almost no experimental studies were made of the mechanism of the hydrolysis of αβ-alkenyl esters until recently.

The molecule of an alkenyl carboxylate, however, contains two reactive centres—the carbonyl group and the vinyl group. The latter, as shown above, is activated by its proximity to the oxygen, so that the hydrolysis of enol acylates can take place in at least two ways: by electrophilic addition to the C=C bond or by nucleophilic addition to the C=O bond. The actual mechanism will depend to a considerable extent on the reaction conditions, in particular the acidity of the medium. In an alkaline medium, in which enol ethers are inactive, primary attack by hydroxide ions at the carboxyl group is most probable. In acidic solutions, attack by protons at the nucleophilic vinyl group becomes equally probable.

αβ-Alkenyl ethers and esters in anhydrous media readily undergo trans-etherification (3) and trans-esterification (4), which in this instance are also described as vinyl exchange:

$$CH_2=CH-OR+XOH\rightleftarrows CH_2=CH-OX+ROH\,, \qquad (3)$$

$$CH_2=CH-OCOR+XOH\rightleftarrows CH_2=CH-OX+RCOOH\,, \qquad (4)$$

where XOH is a compound with a labile hydrogen atom.

Reactions (3) and (4) undergo specific catalysis by the mercury salts of strong acids, whereas in the presence of mineral acids the addition of the reagent XOH takes place chiefly at the ethylenic bond. The mechanism of these reactions will be examined later; here it is important to note the following: (1) catalysis by mercury salts makes it possible to exclude the carbonyl group from consideration as an active centre of the molecule in reaction (4); (2) if the reagent XOH is water, the products of the trans-etherification or trans-esterification are identical with the hydrolysis products, as can be seen from the equation

$$CH_2=CH-OR+HOH\rightarrow ROH+CH_2=CH-OH\rightarrow CH_3CHO \qquad (5)$$

and (3) catalysts for vinyl exchange have also been found to be active in the hydrolysis of vinyl ethers and esters[16-18].

All this leads to the conclusion that in acid hydrolysis and possibly in aqueous hydrolysis the analogy between enol ethers and esters is as valid as that between the esters of enols and the esters of saturated alcohols.

The results of the study of the mechanism of hydrolysis of αβ-alkenyl ethers and esters, given below, have confirmed and refined existing theories of the mechanism of hydrolysis of enol ethers and have shown that existing theories of the mechanism of hydrolysis of enol esters are erroneous.

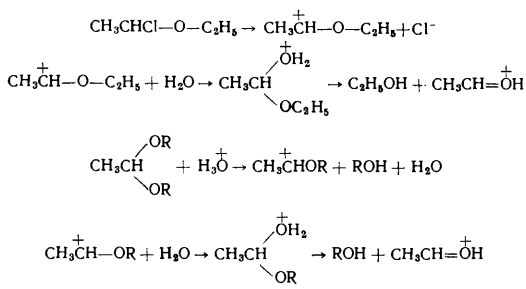
To avoid repetition, we begin with data on the point of fission of the bonds, since this information is necessary in a discussion of any mechanism of hydrolysis of ethers and esters.

2. POINT OF FISSION OF THE BONDS IN HYDROLYSIS

The hydrolysis of ethyl vinyl, n-butyl vinyl, isopropyl vinyl, allyl vinyl, and phenyl vinyl ethers[16], and also 3-ethoxy-2-cyclohexenone[19], in aqueous solutions of sulphuric acid enriched in $H_2{}^{18}O$, gave alcohols which did not contain ^{18}O. "Unlabelled" alcohols were also obtained in the hydrolysis of isopropyl vinyl and α-chlorodiethyl vinyl ethers in neutral solutions, in the hydrolysis of α-chlorodiethyl

ether by sodium carbonate solution[16], and in the acid hydrolysis of acetals[20]. The same result was obtained in the hydrolysis of isopropyl vinyl and n-butyl vinyl ethers, catalysed by mercury sulphate[16]. Thus in the hydrolysis of these alkenyl ethers, bond rupture takes place only between the unsaturated group and oxygen.

On the basis of independent data, the mechanism illustrated by schemes (6) and (7) has been established for the solvolysis of α-halogenoethers[21] and acetals[22]:



(6)

(7)

with the intermediate formation of hemiacetals and their decomposition into carbonyl compounds and alcohols. Data obtained using ^{18}O show that the decomposition of the hemiacetals involves the removal of alkoxy-groups, which during the reaction do not lose their bonds with their oxygen.

Thus the formation of alcohols which do not contain oxygen from the medium, observed in the hydrolysis of vinyl ethers, confirms scheme (1), which assumes the intermediate formation of hemiacetals.

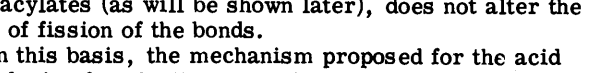
The fact that identical results were obtained regarding the point of fission of the bonds in the hydrolysis of vinyl ethers containing alcohol residues with different structures, such as the ethyl, allyl, and phenyl groups, indicates that the established features are general. This is also indicated by data on the mechanism of the formation of methyl α-naphthyl ether from [^{18}O]methanol and 1-naphthol, catalysed by sulphuric acid, in which the ether contains oxygen only from the methanol[23]. From this it follows that the back reaction in the acid decomposition of this ether should take place with fission of the bond between the unsaturated naphthyl group and oxygen, that is, like the hydrolysis of vinyl ethers.

Study of the acid hydrolysis of enol carboxylates in $H_2{}^{18}O$ showed that in this instance also the reaction involves vinyl–oxygen fission. This was established for the hydrolysis of the following esters: vinyl acetate in acidic and initially neutral media[17,24], vinyl formate, propionate, butyrate, pelargonate, adipate[25], and *p*-methoxybenzoate, isopropenyl acetate and benzoate, α-acetoxystyrene[26], and α-methoxyvinyl benzoate[27]. The same is true of the hydrolysis of vinyl acetate and benzoate[24] and the *p*-methoxy- and *p*-nitro-derivatives of the latter[18] with catalysis by mercury sulphate.

It can be seen from these data that neither the replacement of the alkyl residue by an acyl residue nor the introduction of substituents in the α-position of the vinyl group alters the point of fission of the vinyl group in acid hydrolysis. The point of fission of the bonds is apparently determined primarily by the presence of the ethylenic bond next to the ether oxygen atom.

Fission of the bond between the vinyl group and oxygen in the hydrolysis of enol acylates agrees with the idea that in the presence of electrophilic reagents the active reaction centre is not the carbonyl group but the vinyl group[17,24,27], since solvolytic processes at the carbonyl group are characterised by acyl–oxygen splitting[28,29]. This conclusion is also confirmed by the fact that mercury sulphate—a specific catalyst for electrophilic addition to multiple carbon–carbon bonds—although accelerating the hydrolysis of enol acylates (as will be shown later), does not alter the point of fission of the bonds.

On this basis, the mechanism proposed for the acid hydrolysis of enol esters was the same as that for the hydrolysis of alkenyl ethers[17,24] [see scheme (1)], that is, a mechanism involving hydration of the ethylenic bond [scheme (8)], later confirmed by kinetic data:



(8)

Preliminary addition at the ethylenic bond was also confirmed for the reaction of 1-methoxyvinyl benzoate with $C_6H_5C^{18}O^{18}OH$ without the addition of mineral acid. The ^{18}O is equally distributed between the two reaction products —methyl acetate and benzoic anhydride[30]. Vinyl–oxygen bond fission was also established in the exchange of acetate groups between vinyl acetate and acetic acid in the presence of mercury sulphate[31].

As noted above, enol ethers are stable in the presence of bases, but the ethers of nitrophenols undergo hydrolysis and trans-etherification fairly readily in concentrated alkali solutions. For the example of the alkaline hydrolysis of 2,4-dinitrophenetol, labelled with ^{18}O in the ether group, and the reaction of 2,4-dinitroanisole with $C_2H_5{}^{18}OH$ it was established that during the reaction the alkyl radicals do not lose their bonds with their oxygen atom, that is, only the bond between the aryl group and oxygen is broken[32].

Table 2. Relative* concentration of ^{18}O in the carboxyl group of the acid formed in the alkaline hydrolysis of vinyl esters in the systems: *I*) unlabelled ester + $H_2{}^{18}O$; *II*) ester labelled with ^{18}O in both oxygen atoms + H_2O; *III*) ester labelled with ^{18}O at the oxygen of the C–O–C group + H_2O**.

Vinyl ester	System			Theoretical concentration of ^{18}O for rupture of the bond					
				acyl–oxygen			vinyl–oxygen		
	I	II	III	I	II	III	I	II	III
Acetate	0.32—0.36	0.49—0.50	0.30						
Benzoate	0.39—0.42	0.49	0.34						
Anisate	0.48—0.52	—	0.25	0.50	0.50	0.00	0.00	1.00	1.00
p-Chlorobenzoate	—	—	0.18						
p-Nitrobenzoate	0.45	—	0.28						

* The concentration of ^{18}O in the original labelled compound was taken as unity.

** These esters were prepared by the action of the corresponding acyl chlorides on chloromercuracetaldehyde-^{18}O. It was confirmed for the example of vinyl acetate that the tracer is present only in the ether oxygen atom[35].

In the alkaline hydrolysis of vinyl esters, only part of the ether oxygen appears in the resulting salts of carboxylic acids (Table 2)[17,18,33,34]. At the same time the esters isolated from the reaction mixture after incomplete hydrolysis retain their original isotopic composition. This indicates that isotopic exchange between the ester and the medium does not take place during the reaction, and the results obtained must be attributed to a mixed hydrolysis

mechanism, with fission of the bonds formed by the oxygen atom with both the acyl group and the vinyl group.

The mechanism of the alkaline hydrolysis of enol acylates will be examined in more detail later, in connection with kinetic data. Here we would merely point out that the mechanism of the alkaline hydrolysis of vinyl acetate and vinyl benzoate differs significantly from the mechanism of the alkaline hydrolysis of the ethyl esters of the same acids, since in the hydrolysis of the latter, only acyl–oxygen bond splitting is observed[29].

3. ACIDIC HYDROLYSIS OF ETHERS

After the first systematic studies, which were carried out in Skrabal's laboratory[36–39] with the aim of obtaining quantitative data on the rates of hydrolysis of ethers with the most varied structures, the study of the kinetics of hydrolysis of $\alpha\beta$-alkenyl ethers developed along three directions: (1) investigation of the nature of the catalysis (specific or general acid catalysis); (2) determination of the kinetic isotopic effect of the solvent; and (3) determination of the dependence of the kinetic parameters of the reaction on the structure of the substrate.

With catalysis by mineral acids, the hydrolysis of $\alpha\beta$-alkenyl ethers is described by a first-order equation with rate constants proportional to the concentration of catalyst[40–46]. An exception is the hydrolysis of furan and 2,5-dimethylfuran, for which the kinetic equation contains the acidity function H_0.[47] It should be noted that in the experiments with cyclic ethers the acid concentration amounted to several moles per litre, whereas in the experiments with ethers with linear structure the acid concentration did not exceed 1×10^{-2} N, that is, it was below the limit at which the difference between C_{H^+} and H_0 becomes perceptible. The reaction rate depends to a marked extent on the composition of the solvent, and decreases when dioxan[40] or ethanol[47] are added to the aqueous solutions. The change in the rate of hydrolysis of isopropyl vinyl and n-butyl vinyl ethers with change in the concentration of water in aqueous dioxan solutions from 3 M to 22 M[44] is given by a curve with a minimum in the region of 10 M H_2O, characteristic of changes in H_0 with change in the composition of the medium[48].

The temperature dependence of the rate constants corresponds to the Arrhenius equation[40,43–45]. The activation parameters found from these data are given in Table 3. The values of $\Delta S^{\neq}$ (Table 3) vary from +4 e.u. to −28 e.u., and are linearly related to the activation energy values (only isopropenyl methyl ether does not show this regular feature). This compensation effect is observed if the reaction of the substrate with the solvent makes a significant contribution to the activation parameters of the reaction[49]. With this condition, changes in the value of $\Delta S^{\neq}$ cannot provide a criterion of change in the mechanism of acid catalysis.

The hydrolysis of ethyl vinyl ether[44], isopropenyl methyl ether[43], and 2-ethoxycyclopentene-1-carboxylic acid (ECA)[46] in buffer mixtures with varying concentrations of undissociated acids showed that this concentration appears in the kinetic equation for the reaction, that is, that the hydrolysis of enol ethers undergoes general acid catalysis. The catalytic constants for the proton donors studied are given in Table 4.

The values of k_{HA} given in Table 4 satisfy Brønsted's equation with $\alpha = 0.45$ for ethyl vinyl ether[44] and $\alpha = 0.50$ for isopropenyl methyl ether and isopropyl vinyl ether[43].

General acid catalysis was not observed by Skrabal and coworkers, since they altered the concentration of only one of the components of the buffer mixture, and the increase in the concentration of undissociated acetic acid was proportional to the increase in the H_3O^+ concentration. Recalculation of Skrabal's data[43,44] led to good agreement in the values of $k_{H_3O^+}$ in aqueous solutions, obtained by different authors (Table 4).

Table 3. Kinetic characteristics of the hydrolysis of α,β-alkenyl ethers with catalysis by mineral acids.

No.	Substrate	Catalyst, solvent	$k_{25°}$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	$\frac{k_{H_2O}}{k_{D_2O}}$	References
1	t-Butyl vinyl ether	80% dioxan + $HClO_4$	0.386	7.3	—	—	—	42
2	Isopropyl vinyl ether	80% dioxan + $HClO_4$	0.156	3.0	—	—	—	42
		90% dioxan + H_2SO_4	0.160	—	17.6	−6.0	—	45
		H_2O + HCl	4.45	2.4	14.0	−10.7	—	43
3	Ethyl vinyl ether	80% dioxan + $HClO_4$	0.053	1	—	—	—	42
		40% dioxan + HCl	0.34	—	17.9	−2.6	—	40
		H_2O + $HClO_4$	2.13	—	14.4	−11.1	2.95	44
		H_2O + HCl	1.87	(1)	15.2	−8.2	—	43
4	Isobutyl vinyl ether	80% dioxan + $HClO_4$	0.041	0.8	—	—	—	42
		H_2O + HCl	2.25	(1.2)	15.9	−5.7	—	43
5	n-Butyl vinyl ether	80% dioxan + $HClO_4$	0.037	0.7	—	—	—	42
		80% dioxan + HCl	0.22	—	19.7	—	—	40
		40% dioxan + HCl	0.37	—	19.0	—	—	40
		90% dioxan + H_2SO_4	0.026	—	21.3	+3.9	2.8	45
		H_2O + HCl	2.00	(1.06)	16.2	−4.9	—	43
6	Divinyl ether	H_2O + HCl	0.008	0.004	—	—	—	15
7	2-Ethylbutyl vinyl ether	80% dioxan + $HClO_4$	0.023	0.64	—	—	—	42
8	Benzyl vinyl ether	80% dioxan + $HClO_4$	0.0081	0.15	—	—	—	42
9	β-Chloroethyl vinyl ether	80% dioxan + $HClO_4$	0.0044	0.08	—	—	—	42
		H_2O + HCl	0.165	(0.09)	16.6	−8.5	2.52	43
10	ECA	H_2O + HCl	37	(20)	14.2	−14.2	2.9	46
11	Monovinyl ether of bisethylene glycol	H_2O + HCl	0.40	(0.22)	10.1	−28.3	3.3	41
12	2,3-Dihydropyran	H_2O + HCl	0.27	(0.15)	14.7	−14.7	—	43
13	2,5-Dimethylfuran	H_2O + $HClO_4$	0.0003	$(1 \cdot 10^{-4})$	—	—	1.7	47
14	Vinyl formate	80% dioxan + H_2SO_4	$7 \cdot 10^{-4}$	0.013	15.8	−24.5	0.84	25
15	Ethyl n-propenyl ether	80% dioxan + $HClO_4$	0.0092	0.17	—	—	—	42
16	n-Butenyl ethyl ether	ditto	0.0091	0.17	—	—	—	42
17	Ethyl isobutenyl ether	» »	0.0009	0.017	—	—	—	42
18	β-Chlorovinyl ethyl ether	» »	$8 \cdot 10^{-5}$	0.0015	—	—	—	42
19	Isopropenyl methyl ether	H_2O + HCl	970	(515)	13.6	−1.1	—	43
20	Ethyl isopropenyl ether	80% dioxan + CH_3COOH + CH_3COONa	10000**	—	—	—	—	42

* The rate of hydrolysis of ethyl vinyl ether in 80% aqueous dioxan or in aqueous solution was taken as unity. $k_{rel.}$ values in aqueous solution are given in parentheses.

** The rate constant is too high by a factor of at least 100, since no allowance was made for the catalytic action of the undissociated acetic acid[43].

The general acid catalysis in the hydrolysis of enol ethers indicates unambiguously that the rate-determining stage is the transfer of a proton from the catalyst to the substrate[43], in agreement with the marked decrease in reaction rate in D_2O (Table 3).

In this connection it should be noted that re-examination of the theory of the isotopic effect of the solvent, completed in the early nineteen-sixties, showed that neither the value of $k_{H_2O} : k_{D_2O}$ nor the form of the dependence of the reaction rate on the atomic fraction of deuterium in the solvent

can serve, as was previously supposed, as an unambiguous criterion of the mechanism of acid–base catalysis[50–52]. With independent data on the kinetic role of the stage involving proton transfer, however, the results of the determination of the reaction rate in D_2O and its mixtures with H_2O under certain conditions, in particular for $k_{H_3O} : k_{D_2O} \geq 2$, nevertheless give information on the structure of the intermediate complex and the movement of the proton relative to the reaction coordinate[51,53]. The maximal value of the isotopic effect for reactions with slow proton movement from H_3O^+ is equal to 3.6; this value is reached when in the transition state the proton reacts equally strongly with the water molecule which it is leaving and with the nucleophilic centre of the substrate[53]. This structure of the transition state also corresponds to a value of the parameter α equal to 0.5 in Brønsted's equation[54]. This same parameter can be found from the form of the dependence of the reaction rate on the atomic fraction of deuterium in the solvent using the equation[43,44,55]

$$\frac{k_n}{k_H} = \frac{(1 - n + nl^{1+\alpha})^3 \cdot (1 - n + l^{1+2\alpha} n\, k_D : k_H)}{(1 - n + nl)^3} \qquad (9)$$

where n is the atomic fraction of deuterium and l the exchange coefficient of the ion L_3O^+‡, equal to 0.67.[55] The values of the parameter α found in this way for the hydrolysis of ethyl vinyl ether[44] and 2-chloroethyl vinyl ether[43] were 0.6 and 0.5 respectively, in good agreement with the value found from Brønsted's equation.

Table 4. Catalytic constants for various proton donors in aqueous solution at 25°C.

Substrate	H^+ donor	k_{HA}, litre mole^{-1} s^{-1}	Refs.
Ethyl vinyl ether	H_3O^+	2.13	44
		1.89	43
		2.35*	43
	HCOOH	$8.8 \cdot 10^{-3}$	44
	CH_3COOH	$1.8 \cdot 10^{-3}$	44
		$2.8 \cdot 10^{-3}$	43
Isopropyl vinyl ether	H_3O^+	4.43	43
	CH_3COOH	$8.6 \cdot 10^{-3}$*	
Isopropenyl methyl ether	H_3O^+	970	43
	$H_2PO_4^-$	0.16	43
	HCO_3^-	$8.4 \cdot 10^{-4}$	43
	H_2O	$1.44 \cdot 10^{-6}$	43
2-Ethoxy-1-cyclopentenecarboxylic acid (ECA)	H_3O^+	0.22	46
	$ClCH_2COOH$	0.0026	46

* Recalculated from Skrabal's data[43].

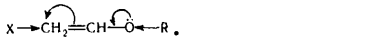
For proton transfer from formic acid to ethyl vinyl ether, $k_{HCOOH} : k_{HCOOD} = 6.8$, compared with 2.95 for catalysis by hydroxonium ions[44]. For the hydrolysis of ECA, the isotopic effect increases from 2.9 for catalysis by H_3O^+ to 8.0 for catalysis by the protons of the carboxyl group of the substrate itself[46]. The explanation of these facts according to modern theories is that the observed influence of the replacement of H by D in solution is made up of two isotopic effects operating in opposite directions: a primary effect leading to a decrease in the reaction rate in D_2O, and a secondary effect leading to an increase in the rate of the process. The secondary isotopic effect is absent if the proton donor contains only one labile H atom[53,56,57].

‡ Where L represents either H or D (Ed. of Translation).

The general acid catalysis in the hydrolysis of enol ethers provides evidence against primary attack by H^+ on the oxygen atom, since this is characterised by rapid attainment of prototropic equilibrium and specific catalysis. Examples of reactions of this type are provided by the hydrolysis of acetals[58] and the alkyl esters of carboxylic acids[29].

Further confirmation of primary attack by the protons on the unsaturated group is provided by the structural dependence of the reactivity of enol ethers in acid hydrolysis. The available kinetic data (Table 3) show that electron-donating substituents attached to the oxygen atom increase the reaction rate (ethers 1–9 in Table 3), whereas the same substituents attached to the β-carbon atom of the vinyl group decrease the reaction rate (ethers 15–18 in Table 3). In both instances, the changes in the hydrolysis rate constants with change in the structure of the substrate are described by the Hammett–Taft equation in the form[42] $\lg(k/k_0) = \sigma^*\rho^*$. An equation of this form indicates that the influence of polar factors predominates. For substituents attached to the oxygen atom, $\rho^* = -2.8$, and for substituents attached to the β-carbon atom of the vinyl group, $\rho^* = +1.5$.

The above data cannot be explained if primary attack by the protons on the oxygen atom is assumed, since in this instance the direction of the influence of the substituents would be independent of their position in the molecule. The influence of substituents indicates that, among the factors determining the reactivity of enol ethers in electrophilic media, the most important part is played by the conjugation of the p-electrons of the oxygen atom with the π-electrons of the double bond. Electron-donating substituents attached to oxygen facilitate this conjugation and increase the reaction rate, but in the β-position of the vinyl group they hinder conjugation and decrease the rate of hydrolysis



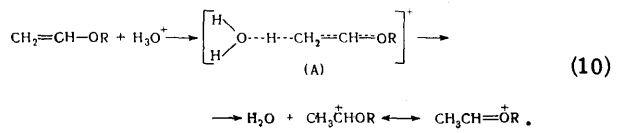
The decrease in the rate of hydrolysis of divinyl ether relative to that of ethyl vinyl ether, which surprised Skrabal, becomes understandable from this viewpoint. Each vinyl group of divinyl ether acts as an electron-accepting substituent relative to the other and weakens its conjugation with oxygen. Comparison of the hydrolysis rate constants for ethyl vinyl ether and divinyl ether, and also for ethyl vinyl ether and vinyl formate, shows that the retarding action of the vinyl group is stronger than that of the carbonyl group, the reaction rate being decreased by a factor of 240 in the first instance and only 80 in the second. Allyl and benzyl groups also show a retarding action, but this is much weaker than that of the vinyl group. The reaction of vinyl ethyl ether is about ten times more rapid than that of 2-chloroethyl ether, but 700 times more rapid than that of β-chlorovinyl ethyl ether. In the first instance the inductive effect of chlorine on the ethylenic bond is shown, whereas in the second instance the effect of conjugation of the free pairs of electrons of the chlorine with the π-electronic system becomes more marked. The chlorine acts as electron donor and hinders the conjugation of the electrons of the oxygen with the double bond.

Not only kinetic data, but also other physicochemical data indicate that electrophilic reagents attack the double bond, and not oxygen. Thus the results of a study of the dielectric constants of solutions of tin(IV) chloride in inert solvents indicate the formation of complexes of two different types on the addition of furan, 2-methylfuran, and thiophen, or the saturated analogues of these compounds[59]. In the first instance, complexes involving the C=C group are

formed, whereas in the second instance complexes involving the oxygen or sulphur atoms are formed. This conclusion was confirmed by spectroscopic data[60] for the example of the complexes of thiophen with tin(IV) chloride.

The analogous study using vinyl ethers was unsuccessful, since these compounds polymerised rapidly in the presence of tin(IV) chloride[59]. Polymerisation itself, however, indicates activation of the double bond, that is, reaction of the complex-forming species with this reactive centre.

The above data provide convincing justification for the mechanism accepted at present for the acid hydrolysis of $\alpha\beta$-unsaturated ethers, according to which the first, rate-determining stage of the reaction involves the transfer of protons from the catalyst to the β-carbon atom of the vinyl group with the formation of carbonium ions[41-47], scheme (10):

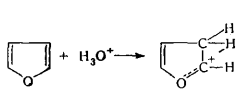


(10)

In the transition complex (A) the proton occupies a central position between the molecules of water and the substrate.

The partial oxonium character of the ions formed, that is, their stabilisation by interaction of the p-electrons of the oxygen with the positive centre, explains the important part played by conjugation and the high reactivity of enol ethers in the presence of electrophilic reagents. In the original state, conjugation of the π-electrons of the multiple bond with the p-electrons of the oxygen leads to localisation of the negative charge on the β-carbon atom of the vinyl group. The corresponding increase in the energy of the original state was recently confirmed experimentally in a determination of the thermodynamic characteristics of the original and final states in the acid hydrolysis of ethyl vinyl ether[61]. The results of this work made it possible to construct the energy profile of the reaction. The presence of the negative charge on the carbon of the vinyl group facilitates attack by protons and the formation of a transition state with structure approaching that of a σ-complex, and not a π-complex. On the other hand, the possibility of displacement of the electrons of the oxygen to the vacant p-orbitals of the neighbouring carbon atom of the carbonium ions leads to delocalisation of the positive charge, and this increases the stability of the ions and makes this reaction path energetically favourable.

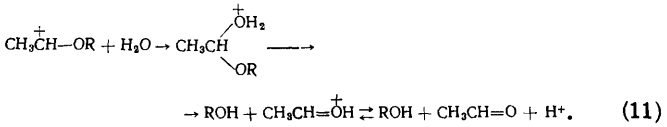
In derivatives of the cyclic vinyl ether furan, the conjugation of the unshared pair of electrons of the oxygen with the π-electrons of the ring does not lead to localisation of the negative charge and an increase in the energy of the original state as a result of the aromaticity of the system produced. The formation of the carbonium ions



is accompanied by loss of aromaticity and a decrease in the conjugation energy. These factors explain the increased stability of furan derivatives in acid hydrolysis, compared with other vinyl ethers, including 2,3-dihydropyran[43]. On the other hand, the increased reactivity of isopropenyl ethers relative to vinyl ethers can be attributed to the increased stability of the carbonium ions with increase in the degree of branching of the carbon chain attached to the positive centre. Carbonium ions with structures similar to those formed in the hydrolysis of enol ethers are formed in the hydrolysis of acetals[58]. In agreement with this, a linear relationship was found between the rate constants for the two reactions with analogous structural changes in the substrate[43].

Kinetic data cannot give information on the subsequent course of the reaction, since the rate-determining stage is the first stage. This gap can be partly filled by using isotopes.

In the hydrolysis of ethyl vinyl ether in D_2O, the acetaldehyde formed contained only one deuterium atom, indicating that the proton transfer is irreversible[44] and that the subsequent transformation undergone by the carbonium ions is more rapid than the isotopic exchange of hydrogen in these ions§. The analogy with the hydrolysis of acetals, and also the results of a study of the mechanism of the acid hydration of alkenes[65], styrene[66], acetylenic ethers, and sulphides[67-69]¶ indicate that the carbonium ions are subjected to nucleophilic attack by water and are converted into the protonated forms of the hemiacetals, which decompose to give the aldehyde and alcohol. The formation of alcohols which do not contain oxygen from the medium in the hydrolysis of both alkenyl ethers and acetals confirms the scheme:



(11)

An interesting feature is that even for allyl vinyl ether, stabilisation of the carbonium ion by attachment of water is more favourable than rupture of the allyl–oxygen bond with the formation of the aldehyde retaining the oxygen of the substrate. This indicates that the $CH_3\overset{+}{C}H-O-CH_2CH=CH_2$ ion is more stable than the allyl cation.

Schemes (10) and (11), based on the results of kinetic and isotopic studies, confirm and give the details of views on the mechanism of the hydrolysis of enol ethers developed on the basis of chemical intuition more than thirty years ago. This now represents one of the few examples where it has been possible to characterise reliably and in sufficient detail the structure of the intermediate complex in the rate-determining stage of the reaction.

4. ACID HYDROLYSIS OF ESTERS

Kinetic data have been published on the acid hydrolysis of esters of four structural types: the vinyl and isopropenyl esters of aliphatic and benzoic acids. It was shown above that change in the structure of enol acylates does not lead to a change in the point of fission of the bonds, which corresponds to the replacement of the anion of the carboxylic acid by hydroxide.

As with the ethers, the acid hydrolysis of enol esters is described by a first-order equation, but it takes place under slightly more severe conditions[25,26,45,70]. The rate constants for the hydrolysis of the alkenyl esters of aliphatic acids in aqueous dioxan solutions are linearly dependent on the analytical concentration of mineral acid. The kinetic equation for the hydrolysis of vinyl and isopropenyl benzoates contains the acidity function H_0 instead of C_{H^+}.[26,45] The problem of whether the acid catalysis is

§ The rapid exchange of the hydrogen of the C–H bonds in carbonium ions is dealt with in papers by Setkina and Kursanov[62,64].

¶ For all these reactions it has been proved that the rate-determining stage is the transfer of H^+ from the catalyst to the substrate with the intermediate formation of carbonium ions.

specific or general has not been studied. The fact that the observed rate constants remain constant with time, that is, as the carboxylic acid accumulates in the reaction system, can be attributed either to the absence of general catalysis or to low values for the catalytic constants of the acids formed, compared with $k_{H_3O^+}$.

The temperature dependence of the rate constants in all instances obeys the Arrhenius equation. The kinetic characteristics of the hydrolysis of the compounds studied are given in Tables 5 and 6.

Table 5. Kinetic characteristics of the hydrolysis of αβ-alkenyl esters of aliphatic acids in aqueous dioxan solutions.

Substrate	Catalyst, solvent	$10^3 k_{80°}$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	k_{H_2O}/k_{D_2O}	Refs.
Vinyl formate	80% dioxan + H_2SO_4	35.5	18.6	15.0	—24.5	0.84	25
	99% dioxan + H_2SO_4	36.7	19.2	13.6	—29.5	1.0	25
Vinyl acetate	80% dioxan + H_2SO_4	4.19	2.19	17.8	—21.0	0.74	45
	99% dioxan + H_2SO_4	1.91	1.0	12.1	—39.6	1.22	45
	50% dioxan + HCl	5.57	2.9	16.2	—25.2*	—	70
Vinyl propionate	80% dioxan + H_2SO_4	1.59	0.83	16.9	—25.8	—	45
	50% dioxan + HCl	3.71	1.9	13.9	—32.5*	—	70
Vinyl butyrate	80% dioxan + H_2SO_4	0.81	0.42	17.5	—25.1	0.70	45
	99% dioxan + H_2SO_4	0.62	0.32	13.8	—32.5	1.3	45
	50% dioxan + HCl	2.43	1.2	15.5	—28.9*	—	70
Vinyl monochloro-acetate	80% dioxan + H_2SO_4	1.43	0.75	14.8	—31.7	—	45
Vinyl adipate	80% dioxan + H_2SO_4	0.90	0.47	18.5	—22.0	—	45
Vinyl phenylacetate	80% dioxan + H_2SO_4	0.71	0.37	19.1	—17.4	—	45
Vinyl trimethylacetate	50% dioxan + HCl	0.41	0.21	23.4	—9.6	—	70
Isopropenyl acetate	80% dioxan + H_2SO_4	1.33	0.70	18.9	—11.7	0.78	26
	50% dioxan + HCl	4.68	2.45	17.5	—21.9	—	70
α-Acetoxystyrene	98% dioxan + H_2SO_4	1.85	0.97	20.0	—16.8	1.06	26

* The rate of hydrolysis of vinyl acetate in 99% aqueous dioxan was taken as unity.

As in the hydrolysis of enol ethers, a compensation effect is observed in the changes in the energy and entropy of activation. The experimental points on the plot of $\Delta S = f(E)$ for vinyl benzoates, the esters of aliphatic acids, and isopropenyl benzoates lie on three parallel straight lines arranged one above the other in the order indicated. Only vinyl formate and isopropenyl acetate do not fit into the general scheme.

In the series of vinyl and isopropenyl benzoates, electron-donating substituents in the *para*- and *meta*-positions of the benzene ring increase the reaction rate, whereas electron-accepting substituents decrease the reaction rate. An exception is vinyl *p*-nitrobenzoate, which reacts more rapidly than vinyl anisate by a factor of several tens. In this example, a departure from simple kinetic orders with respect to substrate and catalyst is also observed. The deviation of vinyl *p*-nitrobenzoate from the general relationship was attributed to a change in reaction mechanism. It is not excluded that the kinetic complications in this instance represent a manifestation of the catalytic activity of the comparatively strong *p*-nitrobenzoic acid.

The logarithms of the hydrolysis rate constants for the benzoates show a correlation with the Hammett constants σ. For the vinyl esters, ρ in the equation $\lg(k/k_0) = \sigma\rho$ is equal to -1.30,[45] whereas for the isopropenyl esters $\rho = 1.1$.[26]

These correlations indicate that the rate of the acid hydrolysis of αβ-alkenyl benzoates is determined chiefly by polar factors. The nature of the influence of substituents is the same as that in the acid hydrolysis of enol ethers, and opposite to that observed in the acid hydrolysis of alkyl benzoates[71].

Table 6. Kinetic characteristics of the hydrolysis of vinyl and isopropenyl benzoates in 99% dioxan at 80°C with catalysis by sulphuric acid.

Substrate,	$10^3 k$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	$\frac{k_{H_2O}}{k_{D_2O}}$	Refs.
Vinyl anisate	0.76	3.5	19.4	—20.5		45
Vinyl benzoate	0.22	1	17.8	—27.0	1.5	45
Vinyl *p*-fluorobenzoate	0.17	0.8	18.6	—25.3	—	45
Vinyl *p*-chlorobenzoate	0.12	0.55	21.4	—18.1	—	45
Vinyl *m*-nitrobenzoate	0.03	0.013	29.0	—3.1	—	45
Isopropenyl anisate	28.8	130	16.1	—22.4	—	26
Isopropenyl benzoate	13.4	60	19.2	—15.1	2.0**	26
Isopropenyl *p*-chlorobenzoate	8.2	37	20.4	—12.5	—	26
Isopropenyl *m*-nitrobenzoate	2.0	9	—	—	—	26
Isopropenyl *p*-nitrobenzoate	2.5	11	22.8	—7.9	—	26

* The rate constant for the hydrolysis of vinyl benzoate in 99% dioxan was taken as unity.

** In 90% dioxan, $k_{H_2O}/k_{D_2O} = 1.80$.

In the series of αβ-alkenyl esters of aliphatic acids, the rate of acid hydrolysis decreases with increase in the length of the hydrocarbon chain of the acid component and with increase in its degree of branching (Table 5). The fact that the decrease in reaction rate is almost the same on going from vinyl acetate to vinyl propionate and vinyl monochloroacetate, in which the acyl residues differ considerably in polarity but have very similar dimensions, and the marked decrease in reaction rate on going to vinyl trimethylacetate[70] indicate that in the acid hydrolysis of these compounds, as in that of the ethyl esters of aliphatic acids, the chief part is played not by polar factors, but by steric factors[25,71].

In accordance with the foregoing, the introduction of a methyl group into the α-position of the vinyl group produces different effects on reaction rate in the benzoates and the esters of aliphatic acids. The change from vinyl acetate to isopropenyl acetate is accompanied by a slight decrease in the rate of hydrolysis, but the corresponding change in structure in the benzoate series leads to an increase in reaction rate by a factor of 40–70. The influence of substituents in the benzene ring is weakened slightly, as can be seen from the decrease in the absolute magnitude of ρ from 1.30 to 1.10.[26]

The esters of aliphatic and benzoic acids also show different behaviour when the H_2O medium is replaced by D_2O. In the first instance, the sign of the isotopic effect of the solvent depends on the concentration of water in the solution. At relatively high concentrations of water (10–20 wt. % in dioxan) the reaction rate in D_2O increases by a factor of 1.2–1.4. Decrease in the water concentration to 1.0–2.0% leads either to the disappearance of the isotopic effect or to a slight decrease in reaction rate in D_2O. The rate of hydrolysis of vinyl and isopropenyl benzoates in heavy

water decreases by a factor of 1.5–2.0, and the retarding influence of D_2O is apparently independent of the concentration of water in the solution[26].

These data show that the kinetic features of the acid hydrolysis of $\alpha\beta$-alkenyl benzoates and ethers are extremely similar and differ significantly from the kinetic features of the hydrolysis of the alkenyl esters of aliphatic acids (influence of substituents, acidity of the medium, and isotopic effect of the solvent). On this basis, the mechanism proposed for the hydrolysis of alkenyl benzoates is the same as that for the hydrolysis of enol ethers[26], with rate-determining transfer of protons from the catalyst to the substrate.

The predominance of not the polar influence but the steric influence of the substituents, the increase in reaction rate in D_2O, and the linear dependence of the rate on the analytical concentration of mineral acid in the hydrolysis of the esters of aliphatic acids can be explained by assuming the A-2 mechanism of acid catalysis, represented by the scheme[26]

$$CH_2{=}CH{-}OCOR + H_3O^+ \rightleftarrows H^+ \cdots CH_2{=}CH{-}OCOR + H_2O$$

$$H^+ \cdots CH_2{=}CH{-}OCOR + H_2O \xrightarrow{\text{slow}} \left[H^+ \cdots CH_2{=}CH{-}OCOR\right]^+ \longrightarrow \quad (12)$$

$$\longrightarrow CH_3CH(OH_2)(OCOR) \longrightarrow CH_3CH{=}\overset{+}{O}H + RCOOH\,.$$

Although the increase in reaction rate in heavy water does not provide unambiguous proof of rapid reversible protonation in the first stage of the reaction, in the present instance evidence in support of scheme (12) is provided by the fact that the isotopic effect of the solvent (Table 5) has the same magnitude as that in other reactions in which the pre-equilibrium stage has been established independently (these values have been summarised[72]). Moreover, the values of $k_{H_2O}:k_{D_2O}$ for the hydrolysis of the esters of aliphatic acids agree with the results of a calculation[72] carried out on the basis of theories regarding a change in the reaction rate constants for acid catalysis in D_2O following the A-2 mechanism[52].

The decrease in the reaction rate in D_2O at low concentrations of water in the solution was attributed[45] to conversion of the open form of the activated complex into the ring form. The marked decrease in the energy and entropy of activation under these conditions (Table 5) agrees with this explanation. It may be assumed that at water concentrations equal to or slightly greater than the concentration of mineral acid, all the water molecules are bound in the solvate sheaths of the protons. This creates stereochemical conditions for the formation of an intermediate complex with a cyclic structure, since it ensures approach of the electrophilic and nucleophilic reagents, joined by hydrogen bonds, from the same direction towards the substrate molecule.

Thus in the acid hydrolysis of enol ethers and enol benzoates, the reaction rate is limited by the first electrophilic stage, leading to the formation of carbonium ions. For this mechanism, steric factors should not influence the reaction kinetics, as was found in the hydrolysis of vinyl and isopropenyl benzoates. The decrease in reaction rate on going from the ethers to the benzoates is in accordance with the weakening of the conjugation of the p-electrons of the C=C bond and the ether oxygen atom under the influence of the carbonyl group. It might have been expected that a carbonyl group situated next to the ether oxygen would make hydrolysis of the enol ethers through carbonium ions energetically unfavourable, since the stabilisation of the carbonium ions as a result of displacement of the p-electrons of the oxygen to the carbonium centre would have led to an improbable structure with two neighbouring electron-deficient atoms.

$$CH_3C(H){=}\overset{\delta+}{O}{-}\overset{\delta+}{C}(=O){-}R \qquad (a)$$

If, however, R is a benzene ring, the positive charge on the carbonyl carbon atom is reduced considerably as a result of the interaction with the π-electrons of the aromatic system. Data confirming the high stability of the benzoyl cations $C_6H_5\overset{+}{C}{=}O$, compared with acetyl and propionyl cations, were obtained in a study of the infrared spectra and NMR spectra of complexes of the corresponding fluorides with Lewis acids[73].

For the alkenyl esters of aliphatic acids, a decrease in the positive charge on the carbonyl carbon atom can take place only as a result of the relatively weak inductive effect and hyperconjugation, and the formation of ions of type (a) becomes unfavourable, and the nucleophilic character of the β-carbon atom of the vinyl group in the original state is decreased. As a result, the electrophilic attack of the protons in the first stage of the reaction does not proceed as far as the formation of a new covalent C–H bond. This process becomes possible only after or at the same time as nucleophilic attack by the water molecules on the α-carbon atom of the vinyl group. Thus the second, nucleophilic stage becomes the rate-determining stage, and this, as indicated above, should be sensitive to steric factors, since it requires movement out of the plane of the bulky acyl and other groups joined to the α-carbon atom, as confirmed experimentally.

Summarising the discussion of the experimental data at present available on the acid hydrolysis of enol ethers and esters leads to the conclusion that a donor–acceptor scheme is applicable in all instances for the mechanism of hydration of the ethylenic bond.

Other conditions being equal, the nature of the limiting stage is related to the structure of the substrate as follows: when structural factors facilitate the stabilisation of carbonium ions, rupture of the double bond and formation of a new C–H bond take place in the first electrophilic stage, which thus determines the rate of the process. Here the chief part is played by factors favouring conjugation of the p-electrons of the ether oxygen and the ethylenic bond. If this conjugation is suppressed, the fission of the old bonds and the formation of new bonds takes place under the simultaneous influence of both the electron acceptor and the electron donor, and the nucleophilic stage of the reaction becomes the limiting stage.

The extension of these ideas to other reactions involving electrophilic addition across the ethylenic bond of vinyl ethers and esters shows that the structure of the latter is not the only factor determining the composition of the intermediate complex and the nature of the limiting stage. Thus the addition of ethanol to butyl vinyl ether and also to vinyl acetate, catalysed by p-toluenesulphonic acid, is described by a second-order equation, in which the concentration of the nucleophile does not appear[74]; this is in accordance with slow transfer of the proton in both instances and is confirmed by the decrease in reaction rate on replacement of C_2H_5OH by C_2H_5OD.

The addition of acetic acid to the same ether and ester is described by a third-order equation, including the concentrations of substrate, catalyst, and acetic acid[74,75].

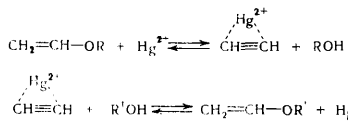
These data, together with the marked isotopic effect for the addition of CH_3COOD, indicate that the reaction mechanism is termolecular.

5. TRANS-ESTERIFICATION AND TRANS-ETHERIFICATION OF VINYL ESTERS AND ETHERS (TRANS-VINYLATION)

The trans-esterification of vinyl esters or the trans-etherification of vinyl ethers formally consists of the transfer of a vinyl group from one alcoholic or acid residue to another—see Eqns. (3) and (4). These reactions are therefore also described as vinyl exchange or trans-vinylation.

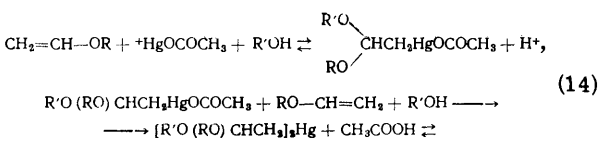
This reaction was first described in the patent literature[1]. Adelman[76] studied vinyl exchange in detail and showed that the mercury salts of strong acids, and also the addition to the reaction mixture of mercury(II) oxide and boron trifluoride, which catalyse the addition of alcohols and carboxylic acids to vinyl ethers and esters, under milder conditions act as specific catalysts for vinyl exchange. It was subsequently established that not only alcohols and acids, but also other organic compounds with a labile hydrogen atom, can take part in this reaction, that the reaction is an equilibrium reaction, and that side-reactions involving addition and polymerisation can be reduced to a minimum if equimolar mixtures of mercury acetate and sulphuric acid are used as catalyst.

For the mechanism of vinyl exchange, Adelman proposed the scheme



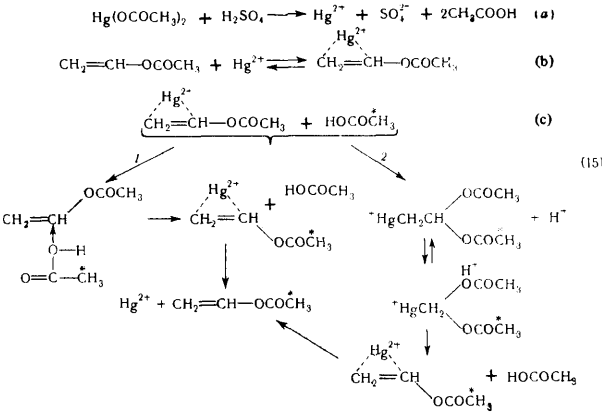
(13)

In 1962 it was established that acid solutions of palladium(II) chloride and salts of other platinum group metals can also catalyse the exchange of acyl residues between vinyl acetate and carboxylic acids and increase the rate of hydrolysis of vinyl acylates[77]. Without giving details of the proposed mechanism, the authors cited suggested that these reactions involve attack on the vinyl ester–metal ion complex by carboxylate ions or water molecules. On prolonged heating, vinyl ethers exchange their alcohol groups for the alkoxy-groups of any alcohols present under the influence of small quantities of mercury acetate in neutral anhydrous media[78]. Good yields of the exchange products could be obtained by removing them by distillation as they were formed. To confirm the suggestion that the reaction involves an organomercury compound, the authors cited showed that the latter catalyse the exchange in the same way as mercury acetate, and proposed the scheme:



(14)

Study of the reaction of vinyl acetate with the two isotopic forms of deuterio-acetic acid CD_3COOH and CH_3COOD at 25°C in the presence of Adelman's catalyst showed that in the reaction with CH_3COOD, deuterium does not enter the vinyl acetate molecule within the time required for the attainment of isotopic equilibrium between vinyl acetate and CD_3COOH.[30] Thus the hydrogen atoms of the vinyl group remain bound to their carbon atoms in the reaction, contrary to scheme (13). This conclusion was also confirmed in a PMR study of the formation of vinyl benzoate from deuterio-vinyl acetate and benzoic acid, catalysed by mercury acetate and BF_3.[12]



(15)

These data unambiguously refute Adelman's mechanism, and also prove that intermediate formation of acylals does not take place in the reactions studied.

Thus for the trans-vinylation of alcohols and carboxylic acids under the influence of the mercury salts of strong acids there remain two possible mechanisms: reversible addition of the cation of the mercury salt and the RO^- or $RCOO^-$ anion across the ethylenic bond, that is, an oxydeoxymercuration mechanism (scheme *15*, *2*) and a mechanism involving direct replacement of one ester group by another in ester molecules activated by coordination to mercury ions, analogous to that proposed by Smidt and coworkers[77] (scheme *15*, *1*).

Both mechanisms assume the formation of ionic complexes of mercury with the vinyl esters (stage *b*) and exchange of ester groups as a result of attack on these complexes by nucleophiles, and both mechanisms show agreement with vinyl–oxygen splitting of the bonds in the ester, confirmed experimentally (see section *2*). According to mechanism (*15*, *2*), the nucleophilic attack is complete with the formation of an organomercury compound. Mechanism (*15*, *1*) makes it possible to avoid this stage. The reaction path is apparently determined by the relative stability of the organomercury compounds and the mercury complexes in each specific instance.

Study of the kinetics of exchange between vinyl acetate and deuterio-acetic acid CD_3COOH under the influence of Adelman's catalyst[79] and the kinetics of the formation of vinyl benzoate from vinyl acetate and benzoic acid with catalysis by mercury acetate and BF_3 [80] showed that the overall order of the reaction with respect to the catalyst depends on the relative concentrations of the mercury salt and the acid. Subsequently, it was found[79] that there is a linear relationship between the reaction rate and the acetic acid concentration (1–10 M) but the initial rate of formation of vinyl benzoate increased more slowly than the benzoic acid concentration (0.3–1.0 M). The reaction with benzoic acid was found to be of first order with respect to vinyl acetate, whereas the exchange with deuterio-acetic acid was found to be of zero order with respect to vinyl acetate. The values found for the Arrhenius activation energy were 9.4 kcal $mole^{-1}$ and 11.0 kcal $mole^{-1}$ respectively.

The kinetic data on the exchange of vinyl acetate with acetic and benzoic acids were obtained under conditions which are not strictly comparable. Firstly, in the works

cited the solvents and acidic reagents used were not identical; secondly, for the exchange with acetic acid the data given were obtained after steady-state conditions had been established, whereas for the exchange with benzoic acid the initial rates of the process were given. Moreover, the ranges of change in the original concentrations in the works cited are narrow and do not always coincide with one another.

The kinetic data on the exchange between vinyl acetate and deuterio-acetic acid were interpreted on the basis of a direct replacement mechanism[78] (scheme *15*, *1*). The chief evidence in support of this scheme was provided by the dependence of the reaction rate on the ratio of the quantities of mercury acetate and sulphuric acid taken; this dependence was incompatible with an oxy-deoxymercuration mechanism. Application of the principle of steady-state concentrations to the corresponding kinetic scheme shows that the reaction rate in this instance would be independent of the acidity of the medium. If, however, the acetoxymercury derivative were formed in concentrations comparable with the concentration of mercury acetate, we would expect the rate to be linearly dependent on the acidity of the medium. The experimental data do not correspond to either situation.

The facts that the reaction rate is independent of the vinyl acetate concentration and that the reaction is of first order with respect to acetic acid do not contradict either of the mechanisms being considered. The linear dependence of the reaction rate on the acetic acid concentration was attributed[79] to rate-determining attack by this reagent on vinyl acetate molecules coordinated to mercury ions. The concentration of the activated substrate, in view of the large excess of substrate relative to the mercury salt, depends only on the latter, so that the concentration of ester does not appear in the kinetic equation.

According to the views of Flid and Temkin[81], the catalytic activity of mercury ions in the reactions of unsaturated compounds is due to the formation of termolecular complexes containing both reagents and the catalyst. From this viewpoint, the slow stage of the process may be the introduction of the reagent with the smaller affinity for the metal ion into its coordination sphere. The dependence of the rate of formation of vinyl benzoate from vinyl acetate and benzoic acid[80] agrees with these views. From published data[80] it can be seen that the initial reaction rate is related to the sum of the concentrations of acetic and benzoic acids†, as would be expected if the slow stage of the reaction is the displacement of one of the molecules of the unsaturated ester from the coordination sphere of the mercury ions by a carboxylic acid molecule.

The difference in the dependence of the reaction rate on the vinyl acetate concentration in the reactions with acetic and benzoic acids can apparently be attributed to the displacement of the equilibrium for complex formation by vinyl acetate with mercury ions towards the starting materials as a result of the lower concentrations of ester and the higher reaction temperature.

Thus although the available kinetic data are insufficient for a final choice to be made between mechanisms (*15*, *1*) and (*15*, *2*), they apparently show better agreement with the first mechanism.

Slinckx and Smets[80] adopted a reaction scheme including the formation of the acetoxy-mercury derivative (*b*) $CH_3COOHgCH_2CH(OCOCH_3)_2$, and they consider that the replacement of the acetate group by the benzoate group takes place in (*b*) as bimolecular substitution at the tertiary carbon atom. As justification for this improbable scheme, which is contrary to extensive experimental material on the behaviour of oxymercury derivatives in acid media[82-84], the authors cited give a kinetic equation of the form:

$$v = k[\text{ester}][C_6H_5COOH][BF_3][(CH_3COO)_2Hg],$$

which does not correspond to their own experimental data, and also the replacement of the acetate group in (*b*) by a benzoate group in the presence of BF_3.[12] This last fact merely confirms again the reversible nature of the deoxymercuration, and cannot serve as proof of the proposed mechanism.

In conclusion it should be emphasised that if the formation of oxymercury derivatives or coordination complexes as active intermediate species in vinyl exchange is determined by the relative stability of these compounds, the second version of the mechanism is more probable for the exchange between vinyl acylates and carboxylic acids, since the stability of organomercury compounds decreases considerably on going from the alkoxy- to the acyloxy-derivatives.

It is not excluded that in the exchange between enol ethers and alcohols the predominating mechanism is that involving the formation of organomercury compounds, as found for vinyl exchange in media not containing a strong acid[78], and also in the hydrolysis of vinyl ethers and esters in the presence of mercury salts, as will be shown below.

6. HYDROLYSIS OF ETHERS AND ESTERS, CATALYSED BY MERCURY SALTS

It was stated above that the addition of a mercury salt increases the rate of hydrolysis of vinyl ethers and esters without altering the point of cleavage of the bonds. Study of the hydrolysis of vinyl acetate and n-butyl vinyl ether in D_2O in the presence of mercury sulphate showed that the acetaldehyde formed contains only one D atom[29], as in the acid hydrolysis of ethyl vinyl ether[43]. The kinetic features of the reaction, which are the same for the hydrolysis of butyl vinyl ether and vinyl acetate[85,86], and also apparently for vinyl benzoates[87], differ significantly from those observed in both acid hydrolysis and vinyl exchange. It was established by a potentiometric method for the example of vinyl acetate and butyl vinyl ether that the addition of mercury perchlorate solution to an aqueous dioxan solution of the ether or ester leads to the formation of acid in quantities equivalent to the mercury salt content[85,86]; this corresponds to quantitative conversion of the mercury salt into an organomercury compound:

$$CH_2{=}CH{-}OR + HgX_2 + HOH \rightarrow XHgCH_2{-}CH\begin{matrix}OR\\OH\end{matrix} + HX$$

or

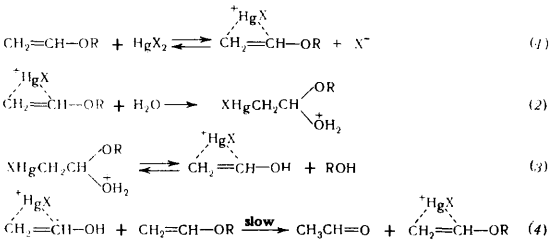
$$CH_2{=}CH{-}OR + HgX_2 + HOH \rightarrow X^- + XHgCH_2CH\begin{matrix}OR\\{}^+OH_2\end{matrix} \rightarrow XHgCH_2CH{=}O + ROH + HX.$$

The rate of hydrolysis increases linearly with increase in the concentration of mineral acid and is independent of the ionic strength of the solution[85,86]. The order of the reaction with respect to the substrate and the mercury salt is fractional and changes with change in the pH of the medium. The ethers and esters can be arranged in the following order of reaction rates at 20°C (the relative rates

† The acetic acid was introduced into the reaction mixture with the mercury acetate solution. The relationship indicated was not noticed by the authors cited[80].

under comparable conditions are given in parentheses): n-butyl vinyl ether (~ 10^2) > vinyl acetate (1.0) > vinyl anisate (0.39) > vinyl benzoate (0.17) > vinyl *p*-chlorobenzoate (0.13) > vinyl *p*-nitrobenzoate (0.10). This order corresponds to an increase in reaction rate with increase in the electron-donating power of the substituent attached to the ether oxygen atom, and is the opposite of that which might have been expected if the reaction rate were determined by the deoxymercuration stage, since organomercury compounds containing acyl groups undergo solvolysis much more readily than their alkoxy-analogues[83,84].

The available experimental data have been explained using scheme (16),[85,86] which is the same for the hydrolysis of vinyl ethers and esters.



(16)

According to scheme (16), the coordination complexes of the ether or ester with mercury ions undergo rapid nucleophilic attack by water and are converted into the oxymercury derivatives. Acid hydrolysis of the oxymercury derivatives does not lead to liberation of the mercury ion catalyst, since the mercury ions remain bound in ionic complexes with the reaction product—the enol form of acetaldehyde. The slow stage of the process is the transfer of mercury ions from the product to the substrate, as shown by stage (4). The transfer of catalyst from the product to new molecules of ether or ester is more rapid, the more nucleophilic their ethylenic bond, in agreement with the observed dependence of the rate of hydrolysis on the structure of the substrate.

Scheme (16), on the one hand, is a detailed form of scheme (*15*, *2*) for aqueous solutions. On the other hand, it corresponds to scheme (*12*) for the acid hydrolysis of the alkenyl esters of aliphatic acids, since the splitting of the double bond takes place under the joint influence of electrophilic and nucleophilic reagents. The difference is that the mercury ions, unlike the protons in acid catalysis, are not regenerated at the end of the catalytic cycle. The greater catalytic activity of mercury ions compared with protons in the hydrolysis of vinyl ethers and esters agrees with the idea that the C=C bond is weakened by dative interaction when the unsaturated ether or ester is introduced into the coordination sphere of mercury ions[88,89].

7. ALKALINE HYDROLYSIS OF ESTERS

The first kinetic study of the alkaline hydrolysis of enol acylates was made in 1927, when Skrabal and Zachorka[90] established that vinyl acetate in alkaline aqueous solutions is hydrolysed much more rapidly than ethyl acetate. They showed that the reaction is described by an equation of second order and of first order with respect to ester and alkali, that is, it is analogous to the hydrolysis of ethyl acetate. The second-order rate constant was found to be 620 litre mole^{-1} min^{-1} at 25°C, which corresponds to an increase in reaction rate by a factor of 100 on going from ethyl acetate to vinyl acetate. The same authors determined the first-order rate constant for the "aqueous" hydrolysis of vinyl acetate, which is equal to 7.4×10^{-6} min^{-1} and is greater than the analogous constant for ethyl acetate by a factor of 1000. According to their data, the maximal stability of vinyl acetate corresponds to pH 4.44.

The vinyl esters of aliphatic acids can be arranged in the following order of rates of hydrolysis at 25°C in a 0.05 *N* solution of sodium hydroxide in 95.5% ethanol[91], analogous to the order for the ethyl and methyl esters[21] (the relative rates of hydrolysis are given in parentheses): monochloroacetate (600) > formate (350) > acetate (1) > butyrate (0.22) > isobutyrate (0.12) > isovalerate (0.085) > crotonate (0.078).

An interesting feature is that under these conditions the rates of hydrolysis of ethyl and vinyl acetates were found to be the same, whereas in the hydrolysis of vinyl acetate in aqueous alkali solution an increase in the reaction rate by more than two orders of magnitude was observed, which is much greater than the increase in the water concentration.

The rates of hydrolysis of the divinyl esters of saturated dibasic acids in aqueous ethanol solutions differ little from that for vinyl acetate. Increase in the length of the hydrocarbon chain leads to a decrease in the reaction rate and an increase in the activation energy[92].

Table 7. Comparison of the kinetic characteristics of the alkaline hydrolysis of vinyl and ethyl carboxylates at 25°C*.

Ester	10^5k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
Vinyl anisate	23.0	18.0	−16.7
Ethyl anisate	11.5	18.6	−15.9
Vinyl benzoate	114	16.9	−17.3
Ethyl benzoate	55.0	17.7	−15.9
Vinyl *p*-chlorobenzoate	371	15.2	−18.5
Ethyl *p*-chlorobenzoate	237	16.8	−16.1
Vinyl *p*-nitrobenzoate	9.25	15.8	−12.3
Ethyl *p*-nitrobenzoate	5.67	14.5	−16.5
Vinyl acetate	1.31	13.0	−26.2
Ethyl acetate	621	14.2	−23.0

* The data on the kinetics of hydrolysis of ethyl benzoate in 85% aqueous ethanol solutions are taken from Ingold and Nathan[93], and the data on the kinetics of the alkaline hydrolysis of ethyl acetate in a solvent with the same composition are taken from Evans and coworkers[94].

The identical influence of substituents in the acyl group of vinyl and ethyl acylates is also confirmed by data on the alkaline hydrolysis of vinyl benzoates with substituents in the *para*-position of the benzene ring in 77% aqueous ethanol solutions[17,34] (Table 7), which show that the similarity in the values of the rate constants for the hydrolysis of vinyl and ethyl benzoates is due to the similarity in the values of the energy and entropy of activation.

The changes in reaction rate in the series of ethyl benzoates, however, is due entirely to change in the activation energy at constant value of the entropy of activation, whereas in the vinyl benzoate series there is an appreciable change in the values of $\Delta S^{\neq}$, which partly compensates the influence of the change in activation energy.

The similarity in the kinetic characteristics of the alkaline hydrolysis of vinyl and ethyl esters (Table 7) apparently is not of great importance from the viewpoint of reaction mechanism, since the results were obtained under

conditions of different water concentration. The marked influence of this factor on the rate of hydrolysis of vinyl acetate was noted above. In the concentration range 5 to 20 M the rate of hydrolysis of vinyl acetate (and vinyl benzoates) is linearly dependent on the water concentration[34], but the influence of the composition of the solvent on the values of $E^{\neq}$ and $\Delta S^{\neq}$ has not been elucidated. Thus the similarity in the values of these parameters for the hydrolysis of vinyl and ethyl esters is possibly due to accidental coincidence. In aqueous solution, the values of $\Delta S^{\neq}$ for the alkaline hydrolysis of $\alpha\beta$-alkenyl and alkyl acetates in some instances differ considerably, although the activation energies are similar (Table 8). For vinyl and ethyl acetates the difference amounts to 17 e.u. The increase in reaction rate by a factor of 30 on going from cyclopentyl acetate to cyclopentenyl acetate is due chiefly to the increase in the entropy of activation.

Table 8. Kinetic parameters of the alkaline hydrolysis of various enol and alkyl acetates in aqueous solution at 20°C.[95]

Acetates	k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Acetates	k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
Vinyl	3.28	12.8	−12.7	Ethyl	0.006	11.0	−31.0
Isopropenyl	0.31	11.6	−21.2	Cyclopropyl	0.18	12.1	−20.8
Cyclopentenyl	0.85	10.5	−24.8	n-Butyl	0.06	10.6	−27.7
Cyclohexenyl	0.18	10.5	−26.5	Cyclopentyl	0.03*	11.8	−28.2

* At 21°C.

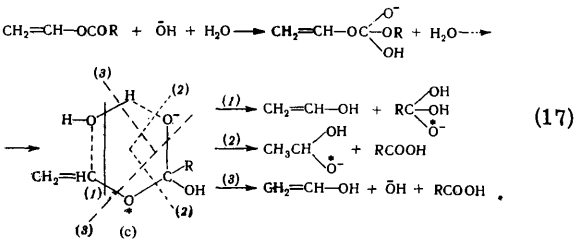
The dependence of the rate constant for alkaline hydrolysis in aqueous ethanol solutions on the structure of the acyl residue satisfies the Taft equation $\lg(k/k_0) = \rho^*\sigma^* + E_S + \psi$ for the vinyl esters of aliphatic acids and the Hammett equation $\lg(k/k_0) = \rho\sigma$ for the benzoates. The values $\rho^* = +2.67$ and $\rho = +2.48$ almost coincide with those established for the alkaline hydrolysis of ethyl carboxylates[17,34].

Change in the structure of the alkenyl radical has a fairly marked influence on the rate of alkaline hydrolysis of enol acylates (Table 8), the effect being apparently stronger than that of analogous changes in the structure of saturated alcohol radicals.

The reaction rate for isopropenyl acetate is smaller by a factor of 10 than that for vinyl acetate, whereas the rate of hydrolysis of isopropyl acetate is smaller than that of ethyl acetate by a factor of only 3.7–4.0;[22,94] according to data obtained by the same authors, the same difference in rates was observed for the hydrolysis of the acetates of primary and secondary butyl alcohols.

The available experimental data are contradictory, since, on the one hand, they indicate a similarity in the mechanism of the alkaline hydrolysis of enol esters and their analogues with a saturated alcoholic group (the stability of the enol ethers in alkaline media and the rapid hydrolysis of the esters, the similarity in the values of ρ in the Hammett–Taft equation for ethyl and vinyl acylates, and the marked similarity in the kinetic parameters for the hydrolysis of ethyl and vinyl benzoates in alcoholic solutions). On the other hand, the partial transfer of the ether oxygen to the carboxyl group in the absence of exchange between the esters and the medium during the reaction, the change in $\Delta S^{\neq}$ when substituents are introduced into the benzene ring of vinyl benzoates, the marked decrease in the reaction rate on going from aqueous to aqueous-alcoholic media, and the more marked influence of the structure of the alcohol component on the reaction rate indicate that the mechanisms of the alkaline hydrolysis of alkenyl and alkyl carboxylates are not the same.

An attempt was made to reconcile the accumulated data by the suggestion that the rate-determining reaction involves attack by hydroxide ions on the carbonyl group with the formation of a cyclic intermediate complex (*c*),[34] similar to that previously proposed by Hinshelwood[96] and by Syrkin and Moiseev[28] for the alkyl esters, scheme (*17*):



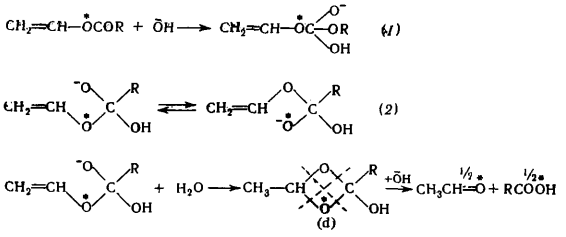
(17)

The authors cited based the proposed scheme on the following considerations: the slow addition of hydroxide ions to the carbonyl carbon atom corresponds to the observed values of ρ and the absence of exchange with the medium during the reaction; the formation of the complexes (*c*) for vinyl esters is facilitated by polarisation of the C=C bond; and decomposition of complex (*c*) in various directions, as shown in the scheme, can lead to the same reaction products with different isotopic compositions. In particular, decomposition in directions *1* and *2* or *3* and *2* at commensurate rates explains the partial transfer of the ether oxygen atom to the carboxyl group of the salt of the carboxylic acid formed.

To this it may be added that the attachment of the oxygen of water to the α-carbon atom of the vinyl group in the transition state agrees with the stronger influence of the structure of the alkenyl group, compared with the alkyl group, on the rate of hydrolysis.

Another possible interpretation of the experimental data appeared recently, since it was established that the hydrolysis of substituted benzhydryl benzoates, in which alkyl–oxygen splitting of the bonds takes place, is accompanied by intramolecular redistribution of ^{18}O between the ether and carbonyl oxygen atoms[97,98]. This was attributed to reversible breakdown of the ester molecule to form ion pairs, whose lifetime in the solvent cell is so great that extensive intramolecular isotopic exchange of oxygen can take place. This reaction path is possible if the structure of the alcohol radical ensures stability of the alkyl cations in the ion pairs.

The structure of the unsubstituted vinyl group does not satisfy this condition, but on the other hand it makes possible exchange between the ester and carbonyl oxygens without the formation of ion pairs, as can be seen from the schemes:

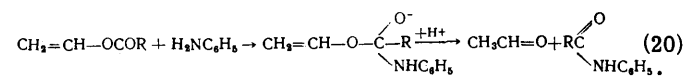


(18)
(19)

In the present instance, this reaction mechanism can be favoured by polarisation of the ethylenic bond. After the formation of the *ortho*-form of the ester, the polarisation

of the double bond should be intensified, and the polarisation is possibly no less than that in the molecules of vinyl ethers.

Evidence in support of schemes (*18*) and (*19*) is provided by the fact that in the acylation of aniline in anhydrous solution by vinyl acetate and benzoate labelled only in the ether oxygen atom, ~ 20% of the tracer was found in the anilides[35]. The following mechanism has been proposed for the acylation of amines by vinyl carboxylates[99]:



(20)

Since the yield of amides is quantitative[99], it is difficult to explain the partial transfer of ether oxygen to the anilide except by using a scheme analogous to scheme (*18*).

For hydrolysis according to scheme (*19*) in a medium enriched in $H_2{}^{18}O$, the concentration of ^{18}O in the anion of the acid formed would be half that in the medium, whereas in the hydrolysis of an ester labelled only in the ether oxygen the concentration would be half that in the original ester, and one-quarter of that in the vinyloxy-group. These relationships were found for the hydrolysis of vinyl anisate (Table 2). It may be assumed that the electron-donating methoxy-group in the *para*-position of the benzene ring facilitates the formation of the cyclic acylal (*d*), since it increases the negative charge on the carbonyl oxygen atom and intensifies the polarisation of the ethylenic bond in the required direction.

All that has been said above regarding the distribution of the tracer in the products of hydrolysis according to scheme (*19*) also applies to scheme (*18*) with the condition that the equilibrium in stage *2* can be established before the decomposition of the *ortho*-form of the ester into the reaction products.

It can be seen from scheme (*18*) that the intramolecular exchange of oxygen may also involve a third oxygen atom of the *ortho*-form. This may explain the data on the isotopic composition of acetic, benzoic, and *p*-chlorobenzoic acids, given in Table 2, particularly if slight exchange between the ester and the medium, which might remain unobserved, is assumed.

We do not yet have sufficient information to enable us to give preference to one of the above schemes. Any interpretation of the mechanism of the hydrolytic decomposition of vinyl esters in alkaline media, however, should take account of the fact that the rupture of the bonds between the vinyl group and oxygen plays a significant part.

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